

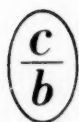
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TABLE OF CONTENTS

		page	Russ. page
1.	On the Nature of Crystals		
3.	The Interatomic Linkage and the Solubility of salts. V. Kurbatov	1337	1333
2.	The Mechanism of Hydration of the Volatile Modification of Phosphoric Anhydride. N. I. Rodionova and Yu. V. Khodakov	1401	1347
3.	The Physico-chemical Investigation of Iodine Solutions. VII. The System Nickel Hexammino Iodide - Iodine. Ya. A. Fialkov and F. D. Shevchenko	1413	1358
4.	An Investigation of the Ternary System of Calcium, Potassium and Sodium Nitrates in Melts. P. I. Protchenko and A. G. Bergman	1421	1365
5.	On the Autoactivation of Zinc Sulfide. B. M. Gugel	1433	1376
6.	The Reduction of Silicotungstates with Hydrogen. I. Potassium Tungsten Bronze. E. A. Nikitina and A. S. Kokurina	1437	1380
7.	I. The Mechanism of Oxidation of Nitric Oxide in Different Discharges. T. V. Zabolotsky	1441	1384
8.	II. The Mechanism of Oxidation of Microconcentrations of Nitric Oxide in the Corona Discharge. T. V. Zabolotsky and S. N. Solniskova	1445	1388
9.	III. The Catalytic Role of Ozone in the Oxidation of Nitric Oxide. T. V. Zabolotsky	1449	1392
10.	The Inapplicability of Bodenstein's Kinetic Equation to the Oxidation of Nitric Oxide under Dynamic Conditions. T. V. Zabolotsky	1451	1394
11.	The Complex of Univalent Copper with Thiocyanate. I. A. Korshunov and N. I. Malyugina	1455	1399
12.	The Classification of Complex Formers and Addends on the Basis of their Energy Characteristics. K. B. Yatsimirsky	1461	1404
13.	The Pentaamino Formates of Cobalt (III). K. B. Yatsimirsky	1465	1408
14.	Complex Compounds of Iron, Aluminum and Chromium with Pyramidon. T. E. Gulyaeva	1469	1412
15.	The Nomenclature of the Most Important Silico-organic Compounds. A. P. Kreshkov	1473	1415
16.	The Viscosity of the Systems Formed by Benzene and its Homologs with the Lower Alcohols. B. Ya. Teitelbaum, T. A. Gortalova and S. G. Ganelina	1481	1422
17.	The Alkylation of Acyl Derivatives of Aromatic Amines by the Friedel Crafts Reaction. 2. The Alkylation of Acetanilide. G. S. Kolesnikov and T. V. Smirnova	1487	1427
18.	Derivatives of Acetylene. 114. The Mechanism of Hydration and Cyclization of the Dienines. XXIII. The Synthesis of 1,2-Di-(p-hydroxyphenyl)-3-methyl- $\Delta^{1,2}$ -Cyclopentene-5-one by the Method of Hydration and Cyclization of the Dienines. I. N. Nazarov and I. L. Kotlyarevsky	1491	1431
19.	Derivatives of Acetylene. 115. The Mechanism of Hydration and Cyclization of the Dienines. XXIV. The Hydration of 5-Phenyl-6-Methyl-1,5-Heptadien-3-ine to give 5-Phenyl-6-Methyl-1,5-Pentadien-4-one, and its Cyclization to give 1-Phenyl-2,2,3-Trimethyl- $\Delta^{3,4}$ -Cyclopenten-5-one. A New Type of Cyclization of Substituted Vinyl Allyl Ketones, which do not have Free Hydrogens in the Vinyl Radical. I. N. Nazarov and I. L. Kotlyarevsky	1501	1441
20.	Derivatives of Acetylene. 116. The Mechanism of the Hydration and Cyclization of the Dienines. XXV. The Hydration of 5-Tert. Butyl-6-Methyl-1,5-Heptadien-3-ine and the Cyclization of the 5-Tert. Butyl-6-Methyl-1,5-Heptadien-4-one thus Formed to give 1-Tert. Butyl-2,2,3-Trimethyl- $\Delta^{3,4}$ -Cyclopenten-5-one. I. N. Nazarov and I. L. Kotlyarevsky	1509	1449
21.	The Condensation of Oleic Acid with Formaldehyde. G. V. Pigulevsky and M. G. Tatarskaya	1517	1456
22.	On the Action of α and γ -Bromoacetic Esters and of 2-Chlorocyclohexanone on the Ethyl Ester of Phosphorous Acid on Sodium Diethylphosphite. B. A. Arbuzov, B. P. Pugovkin and N. P. Bogomostseva	1529	1468
23.	The Question of the Methods of Preparation of β -(Naphthyl-1) Acrylic Acid and its Ethyl Ester. S. I. Sergievskaya, K. V. Levshina and E. N. Petrova	1539	1478
24.	(5-Nitronaphthyl-1)-Propiolic Acid and its Transformations. S. I. Sergievskaya, K. V. Levshina	1543	1481
25.	On the $\alpha, \alpha', \alpha''$ -Trivinyltrialkyl Esters of Phosphorous Acid. N. A. Chafaeva, Gilm. Kanay	1549	1487
26.	XXVIII. A Comparison of the Activities of Ammonia and Aniline in the Reaction with Furan and Furanidine. Yu. K. Yuriev, I. K. Korobitsina and M. I. Kuznetsova	1555	1493
27.	On 1,3-Dimethylcyclopentane. A. V. Koperina, L. M. Nazarova and B. A. Kazansky	1561	1498

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ON THE NATURE OF CRYSTALS

3. THE INTERATOMIC LINKAGE AND THE SOLUBILITY OF SALTS

V. Kurbatov

The value of interatomic linkage can, as has been shown in previous papers [1], be calculated from the formula:

$$K_{cr} = 0.5 C_{cr} \frac{d_0}{\beta_t}$$

Where C_{cr} is the heat capacity of the crystal, d is the density at 0° , $\beta_t = 3\alpha_t$, the cubic coefficient of expansion. It has been shown by direct comparison that in the case of elements this value changes according to certain rules in the subgroups of the Mendeleev system, and therefore, that it is related to the chemical properties of substances and at the same time to such calculated typically physical and even mechanical properties as the hardness according to Hertz-Brinel and the melting point. Thus, it has been shown that a typically mechanical property is directly related to the chemical structure of a substance. This has later been confirmed for acids, sulfides, halides, and oxides. At the same time it has been shown by a review of the values of K_{cr} for organic compounds that the values of K_{cr} correspond completely to the solubilities of organic compounds in each other as arranged on the basis of isofluid type. This is also confirmed by the insolubility in water of the majority of organic compounds which do not possess innogenic groups like CO, COOH, NH_2 , NO_3 , etc. Thus, the solubility is determined not so much by the closeness of the dimensions of the molecules as by the degree of difference between the reactions of the molecules of each type with each other. While all the micromolecules of water are capable of exchanging ions with each other: $H-OH + H-OH \rightleftharpoons H-OH + H-OH$, to form macromolecules, the micromolecules of methane are almost completely incapable of exchanging ions and forming macromolecules. Therefore, when mixing takes place, as a result of the external application of mechanical energy to water and methane, or, to take a more obvious case, to water and hexane, the micromolecules of water are strongly attracted to each other, as if they were squeezed out of their macromolecules by the hydrocarbon. The solution of salts in water, that is, of typically ionic substances similar to water, is quite another thing despite the fact that their ions may be very considerably different from the ions of water, like $[Fe(CN)_6]^{---}$, $[Co(NH_3)_6]^{+++}$, etc. It is obvious that in the case of salts and of electrolytes in general, in order to have the possibility of solution in water there must be a preliminary formation of ionic hydrates. In this case, the phenomenon of salt solution, as was shown long ago (V. Kurbatov, 1924) is very complicated. It may be divided into at least three steps:

- 1) The hydration of the surface ions,
- 2) the penetration of water through the aqueous canals of the surface lattice

to deeper layers of ions,

3) the rupture of the surface hydrated ions with the simultaneous hydrolysis of the salt and the "halization" of the water.

T A B L E 1
Interatomic Linkage of Crystals of Oxygen Salts

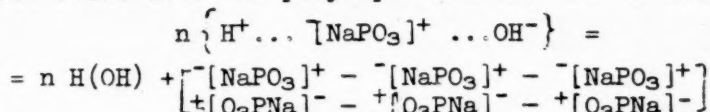
	C	d	$\beta_t = 3\alpha$	K_{cr}
NaNO ₃	0.278	2.25	0.0 ₃ 21	51000
KNO ₃	0.239	2.11	0.0 ₃ 23	45000
NH ₄ NO ₃	0.407	1.71	0.0 ₃ 152	94000
AgNO ₃	0.144	4.35	0.0 ₃ 22	59000
Na ₂ HPO ₄ (780°)	0.257	1.53	0.0 ₃ 053	160000
NaPO ₃ (650°)	0.217	2.48	0.0 ₃ 043	258000
KMnO ₄	0.179	2.70	0.0 ₃ 27	34000
KIO ₃	0.116	3.89	0.0 ₃ 092	77000
KClO ₃	0.196	2.34	0.0 ₃ 25	45000
K ₂ SO ₄	0.199	2.67	0.0 ₃ 13	90000
(NH ₄) ₂ SO ₄	0.265	1.77	0.0 ₃ 112	36000
Rb ₂ SO ₄	0.123	3.61	0.0 ₃ 109	84000
Cs ₂ SO ₄	0.0998	4.26	0.0 ₃ 105	83000
Ag ₂ SO ₄	0.141	4.35	0.0 ₃ 065	195000
K ₂ Cr ₂ O ₇	0.184	2.70	0.0 ₃ 113	91000
K ₂ CO ₃	0.216	2.04	0.0 ₃ 14	65000
K ₂ SiO ₃	0.199	2.73	0.0 ₃ 31	57000
(NH ₂) ₄ P ₂ O ₄	0.347	1.61	0.0 ₄ 9	128000
(NH ₄) ₂ HPO ₄	0.38	1.62	0.0 ₃ 17	75000
(NH ₄) ₃ PO ₄	0.409	1.45	0.0 ₃ 25	55000
Sr(NO ₃) ₂	-	-	-	72000
Ba(NO ₃) ₂	0.113	4.5	0.0 ₃ 062	116000
SrSO ₄	0.143	3.96	0.0 ₄ 62	190000
BaSO ₄	0.113	4.5	0.0 ₄ 53	174000
Boracite	0.344(?)	2.9	0.0 ₅ 97	2000000
MgCO ₃	0.914	3.06	0.0 ₄ 35	605000
CaCO ₃ (calcite)	0.201	2.75	0.0 ₄ 159	716000
CaCO ₃ (aragonite)	0.206	2.95	0.0 ₄ 579	201000
(MgFe)CO ₃	0.214	3.06	0.0 ₄ 36	390000
FeCO ₃	0.183	4.0	0.0 ₄ 35	540000
Azurite	0.057	3.83	0.0 ₄ 316	143000
Mg(AlO ₂) ₂	0.19	3.8	0.0 ₄ 154	975000
(MgFe)(AlO ₂) ₂	0.17	3.55	0.0 ₄ 157	790000
Fe(FeO ₂) ₂	0.168	5.18	0.0 ₄ 219	840000
(FeZnMn)[(Fe,Mn)O ₂] ₂	0.115	3.14	0.0 ₄ 231	330000
Zn(AlO ₂) ₂	0.138	4.3	0.0 ₄ 156	810000
Diopside	0.191	3.32	0.0 ₄ 231	570000
Amphibole	0.196	3.41	0.0 ₄ 186	513000
Augite	0.191	3.32	0.0 ₄ 231	569000
Phenacite	0.289	2.99	0.0 ₅ 75	2370000
Zircon (ZrSiO ₄)	0.145	4.25	0.0 ₄ 181	1530000

In actual fact, the phenomenon is considerably more complicated, as was shown in the paper "The Interatomic Linkage of Oxides and Sulfides," because of the formation of polyions and polyamphions. But with oxides this is the case of one of the ions, while with salts this is possible for both if their ionic or coordination

valences are sufficiently high.

The calculated values of K_{Cr} for salts, from the values of β_t , \underline{d} , and C_{Cr} , now known, are collected in Table 1.

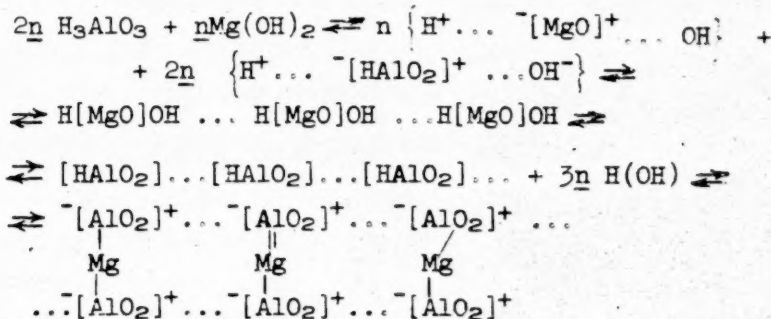
It is clear from Table 1 that K_{Cr} for typical salts such as $NaNO_3$, KNO_3 , $AgNO_3$, $KMnO_4$, KIO_3 , $KClO_3$... is either almost equal to, or less than K_1 for water (75,000). The values are somewhat higher than the K_1 for water for mono-divalent and mono-trivalent salts such as K_2SO_4 , $(NH_4)_2SO_4$, Rb_2SO_4 , Cs_2SO_4 , $K_2Cr_2O_7$, $(NH_4)_3PO_4$, and even lower for K_2CO_3 and K_2SiO_3 . K_{Cr} is low for the mono-trivalent $(NH_4)_3PO_4$ and for the incompletely substituted $(NH_4)_2HPO_4$. The fairly high value for NH_4NO_3 may be due to the influence of polymorphic changes which have not been completed. On the other hand, the very high value K_{Cr} (250,000) for $NaPO_3$ is of course related to the polyamphion structure of this salt, i.e.



The same reason explains the increased values of K_{Cr} for



Of the divalent salts, the most soluble $[Sr(NO_3)_2]$, $[Ba(NO_3)_2]$ have, in anhydrous condition, a value of K_{Cr} somewhat higher than the K_1 of water, and the very slightly soluble ones ($SrSO_4$, $BaSO_4$) have a value 2.5 times as great as the K_1 of water. The insoluble $MgCO_3$ and $CaCO_3$ have values 5 to 10 times as great. The K_{Cr} for spinels is in general above 800,000, a fact which indicates the lack of correspondence of the structure of the spinels to the formula $Mg(AlO_2)_2$, as previously proposed, or to $Al_2[MgO_4]$ with the anion $(MgO_4)^{--}$, as has been proposed in relation to this structure. In actual fact, the spinels have a face-centered cubic structure starting from Mg and Al (in the case of the magnesium-aluminum spinels). In these, the Mg has 4 oxygens around it at equal distances, and the aluminum 6 oxygens at almost equal distances, or in other words, the tetra-coordinated Mg and the hexacoordinated Al have almost the same importance in the formation of the lattice, which is obviously not of the salt type (that is, not the result of opposing charges) but of the gel type, or that of the type produced by the reaction of aluminates with silicates in the industrial formation of permutites



In accordance with this same idea, $K_2Cr_2O_7$ and the ion $[Cr_2O_7]^{--}$ actually exist only in the form of $2H(CrO_3)OH = HCH + [-(CrO_3-O-CrO_3)]^-$.

From this same Table 1 we see that K_{Cr} for mono-monovalent salts does not exceed 100,000; we saw that was also true of the halides.

Salts with bi-monovalent and mono-bivalent ions have K_{Cr} of the order of 100,000 to 125,000 atm. Salts of the bi-bivalent type have an internal pressure from 200,000 to 600,000 atm., as can be seen from Table 2.

TABLE 2

The Limiting Values of K_{cr} . for Anhydrous Salts with Ions of Equal Valence

1-1 Valent	30000 - 60000
1-2 Valent	90000 - 120000
2-1 Valent	80000 - 120000
2-2 Valent	200000 - 600000
2-3 Valent	750000
Spinels	800000 - 1000000
Silicates with bivalent cations..	500000 - 600000
Phenacite	2400000
4-4 Valent zircon	1500000

The K_{cr} . of apatite $[Ca Ca_3(PO_4)_2]F_2$ is more than 5 times as great as that of $Ca_3(PO_4)_2$, as the result of the great ability of the fluorine to enter into the formation of complexes.

Boracite is a unique and extremely complicated mineral, $Mg_7Cl_2B_{10}O_{36}$, which is built up of twenty-four pyramids, joined together at the peaks in a twenty-four-faced cubic syngony. The data for it do not permit us to be certain whether the low coefficient of expansion is the result of the manner in which these are joined or is actually the coefficient of expansion of the monoclinic crystals.

Thus, a K_{cr} . of the order of 350000 atm (and higher) is sufficient for the coordination of the water molecules around the ions of the salt, but in a number that will make the breaking away of the ions into the water impossible, and the salt will be insoluble. It is very probable that the limit of the value of the interatomic linkage needed to prevent solubility is different for ions with different degrees of hydration and is related to the value of the intermolecular linkage of water, as a result of which the salt ions are broken away from the strongly hydrated crystal or even from a crystal which has been converted into a gel.

TABLE 3

Relation between K_{cr} . and the Melting Point of Salts

	K_{cr} .	M.p.	$K_{cr} : m.p.$		K_{cr}	M.p.	$K_{cr} : m.p.$
NaCl	77000	1073°K	71	K_2SO_4	102000	1340°K	76
KCl	58000	1097	55	K_2CO_3	36000	1164	32
KBr	51000	1000	51	$Sr(NO_3)_2$	72400	918	78
KI	36000	966	37	$Ba(NO_3)_2$	116000	865	130
$NaNO_3$	51000	550	90	$Ca_3(PO_4)_2$	90000	1823	50
KNO_3	45000	610	74	Augite	569000	1380	410
NH_4NO_3	94000	438	22	Amphibole	543000	1550	330
$KClO_3$	45000	643	71	Phenacite	2370000	2300	1000
KIO_3	77000	633	120	$Mg[AlO_2]_2$ n ...	985000	2200	440
K_3PO_4	54000	1613	44	$Fe[FeO_2]_2$ n ...	840000	1530	560
$K_2Cr_2O_7$..	140000	662	220				

It has been previously pointed out that for halide compounds too the ratio $K_{cr} : m.p.$ fluctuates within comparatively narrow limits. For all salts except the bi-monovalent this ratio is close to 20 and for the bi-monovalent it is close to 70. If the data for silicates and aluminates are removed from Table 3, which contains a comparison of this same ratio for oxygen-containing salts, the $K_{cr} : m.p.$

has an average value of 57, and for the silicates and aluminates the same ratio is about 590, that is, about 10 times as great. This can only be explained by the fact that the character of the process of melting is essentially different with the latter than with salt compounds that is, by the assumption that the crystals of silicates and aluminates are limiting cases of gels, and that therefore their melting begins with the transformation into a liquid intercrystalline polyamphion mass, that is into an anode skeleton filled with cells. In the case of beryl, for instance, there would appear to be such portions where the BeO is bound to $(\text{SiO}_4)_n$ and $(\text{AlO}_3)_n$ groupings. Thus, the decomposition of the crystal lattice which proceeds with individual micromolecules of salt compounds, takes place in the case of silicates and aluminates with entire crystal polyions.

A comparison of K_{cr} with the mineralogical hardness (B_m) can be carried out for a relatively small number of minerals.

T A B L E 4

Ratio of Interatomic Linkage to the Hardness of Salts

	K_{cr}	Hardness B_m	$K_{cr}:B_m$
NaCl	77000	30000	2.5
KCl (sylvite)	58000	29000	2
NH_4Cl	59500	29500	1.9
AgCl	105000	70000	1.5
AgBr	74000	65000	1.25
CaF_2	249000	76000	3.3
KNO_3	54000	27000	2
$(\text{NH}_4)_2\text{SO}_4$	112000	56000	2
SrSO_4	210000	60000	3.5
BaSO_4	230000	64000	3.5
MgCO_3	605000	140000	4.5
CaCO_3 (calcite)	635000	210000	3
CaCO_3 (aragonite)	201000	50000	4.0
FeCO_3	543000	140000	3.85
Azurite	143000	38000	4
Spinel	980000	120000	8
Corundum	1100000	120000	9.0
Quartz	365000	50000	7.0
Phenacite	2378000	300000	8.0
Zircon	1950000	250000	7.5

In view of the difficulty of obtaining sufficiently reliable data for the hardness, and in view of the considerations above with regard to the infiniteness of the hardness, it would be wrong to expect the ratio of $K_{cr}:B_m$ to be constant. However, it can be seen from Table 4 that this ratio for salts of mono-monovalent ions which do not form stable coordination complexes (K^+ , Na^+ , Cl^- , NO_3^-), equals $29,000 \pm 7\%$. For salts of mono-monovalent ions which give stable complexes (AgCl, AgBr), it equals $67,000 \pm 3\%$. For salts of bi-mono and mono-bivalent ions such as CaF_2 , $(\text{NH}_4)_2\text{SO}_4$, it equals $66,000 \pm 13\%$.

$K_{cr}:B_m$

bi-bivalent salts (slightly soluble)
tri-trivalent salts
quadri-quadrivalent salts

$175,000 \pm 20\%$
 $1,000,000 \pm 30\%$
 $1,000,000 \pm 50\%$

There is no doubt that the mineralogical hardness, that is, the difficulty of breaking away the surface ions, sharply increases in comparison with K_{cr} as the valence of the ions increases. This indicates the incorrectness of the calculated values of the mineralogical hardness, as a transition, by the scale of Moos, from 8 to 10 should actually be expressed by an increase not of 25% but of a thousand times.

The mineralogical hardness of a crystal, that is, the force necessary to break off the surface micromolecules of the crystal (abrasion) depends on the stability of the linkage of the surface ions, and is related to the incompleteness of the number of surrounding ions when compared with the number of ions which are coordinated around an ion of the same charge inside the crystal. We must recall that when the first atom is broken off, as from the corner of a cube, an octahedral side is formed along with three new corners, while when atoms are broken off from the ideal edge of a cube the side of a dodecahedron is formed, that is, as we pass to blunter angles and to new corners and edges, it becomes more and more difficult to break these off. Therefore, the method of abrasion (Moos) is a very conditional one. It is clear that there is not necessarily any parallelism between the changes of the mineralogical hardness and of K_{cr} , or between the solubility and the mineralogical hardness. However, when we make the transition from salts with ions of lower valence to salts with ions of higher valence, both K_{cr} and the mineralogical hardness increase, and the solubility decreases, as is evident from Table 5.

TABLE 5

Relation between Valence, Solubility, and Weight of Cations (t about 20°)

1-1-valent ions	NaCl	KCl	RbCl	CsCl
Solubility	0.45	0.34	0.4	0.38
2-1-valent ions	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
Solubility	0.39	0.38	0.24	0.13
2-1-valent ions	MgCl ₂	ZnCl ₂	CdCl ₂	HgCl ₂
Solubility	0.38	0.52	0.27	0.26
1-2-valent ions	NaSO ₄	K ₂ SO ₄	Rb ₂ SO ₄	Cs ₂ SO ₄
Solubility	0.23	0.057	0.10	0.18
2-2-valent ions	MgSO ₄	CaSO ₄	SrSO ₄	BaSO ₄
Solubility	Very great	0.009	0.000005	0.0000009
2-2-valent ions	MgSO ₄	ZnSO ₄	CdSO ₄	HgSO ₄
Solubility	Very great	0.26	0.21	Hydrolysis

Although during the process of solution the first atoms are broken off from the corners, and the next atoms from the edges, all the same the value of the solubility is determined, when sufficiently large crystals are present on the bottom, by the ratios between the values of the attraction of the ions into the solution on the one hand, and the interatomic linkage of the crystals on the other.

In Table 5 there is a comparison of the values of solubility in gram-moles of salt per 100 parts of solution. From this it is clear that the assumption that the solubility decreases in a subgroup as the weight of the cation increases is correct, and that therefore the solubility decreases as the degree of hydration decreases. An increase in hydration in going over from one group to another in a given series of the Mendeleev system means an increase in solubility. As has been shown above (as, for example, by comparing the values of K_{cr} for spinels), when it comes to salts of oxygen-containing acids with the very highest valences, the transition from solution to crystal takes place by way of a gelatinous state. Therefore the processes of solution and crystallization of these salts, and probably of all salts, must be considered to be even considerably more complicated than

has been indicated above, as for example in the case of CuSO_4 .

TABLE 6

Scheme of Solution and Crystallization of Anhydrous Salts

Stage	Anhydrous CuSO_4 crystal	Water $[\text{H}(\text{OH})]_n$	Stage
I	First stage of hydration $\text{Cu}[\text{SO}_3(\text{OH})_2]$	Water $[\text{H}(\text{OH})]_{n-1}$	VIII
II	Second stage of hydration $[\text{Cu}(\text{H}_2\text{O})_2][\text{SO}_3(\text{OH})_2]$	Water $[\text{H}(\text{OH})]_{n-3}$	VII
III	Third stage of hydration $[\text{Cu}(\text{H}_2\text{O})_4][\text{SO}_3(\text{OH})_2]$	Water $[\text{H}(\text{OH})]_{n-5}$	VI
IV	$[\text{Cu}(\text{H}_2\text{O})_6][\text{S}(\text{OH})_6]$	Water $[\text{H}(\text{OH})]_{n-10}$	V
V	Gelatinous condition of coagulation, fundamentally precrystalline	Water $[\text{H}(\text{OH})]_{n-x}$	IV
VI	Gelatinous condition of coagulation with very little incipient crystallization	Water $[\text{H}(\text{OH})]_{n-z}$	III
VII	Gelatinous condition of entire mass if insufficient solvent		II
VIII	Uniform solution		I

We may note at this point that the hydration of the ions, or their coordinating action on the water, increases as the valence of the ions increases, that is, as there is a transition in the Mendeleev Table from Group I to Group VII. But it decreases as the atomic weight in each subgroup rises in proportion to the increase in the ability to give lower values of the valence, that is, as the stability of the compounds at the higher valences decreases. With regard to this point, the solubility of single-type salts decreases during the transition to the heavier atoms, and this is particularly evident from a comparison of the valence and the solubility in Table 5. It is self-evident that if the number of molecules of water-solvent is too small, then when there are many hydrated ions, and the number of coordinated water ions around each one is great, the solubility may be lowered because of the fact that there is an insufficient number of water ions around each hydrated ion to attract it.

The phenomena of solution and solubility are still more complicated when the hydration is very great, as for example with trivalent ions, as can be seen from the following comparison:

	AlCl_3	GaCl_3	InCl_3	FeCl_3
Solubility:	0.31;	Deliquesces;	Deliquesces,	0.11,
	$\text{Al}_2(\text{SO}_4)_3$	$\text{Ga}_2(\text{SO}_4)_3$	$\text{In}_2(\text{SO}_4)_3$	$\text{Tl}_2(\text{SO}_4)_3$
Solubility	0.67	Deliquesces	(?)	0.007

Between the appreciably soluble salts like BaSO_4 (0.000009 equivalents per liter), Ag (0.0515 equivalents per liter) and those completely insoluble in pure

water, such as calcite and magnesite, the difference in values of K_{Cr} is very great.

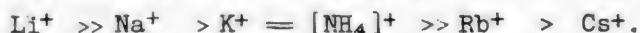
	K_{Cr}	Solubility
AgCl	105000	0.00000018
SrSO ₄	228000	0.000005
BaSO ₄	211000	0.0000009
CaCO ₃ calcite	640000	0
MgCO ₃ magnesite	605000	0
FeCO ₃ limonite	540000	0

Thus the solubility is determined not only by the value of K_{Cr} of the crystal, but also by the stability of the compounds formed by the ions and water, or in other words, by the extent to which the coordination of the molecules of water around the ion penetrates into the surrounding water-solvent, and at the same time by the stability with which the water is held by the salt ions in the crystal hydrates which are formed, as can be seen from the following comparison:

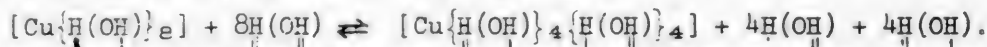
The ability to coordinate water molecules around the ions of the salt:



The ability to form crystal hydrates:

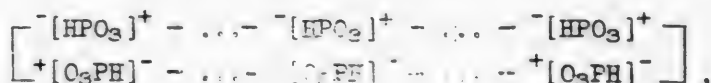


However, it does not follow from this that the solubility of lithium salts is always greater than that of sodium salts. The fact is that the hydrated ions are drawn into the water as a result of the exchange of the molecules of water or the ions of water which enter into the composition of the coordination hydrates with the ions of solvent water, as for example:



The formula $[Cu(HOH)_8]$ is here advanced as a hypothetical one; however, it is close enough to such examples as the crystal hydrate $NaOH \cdot 7H_2O$ to show that the ions in solution are attached to a much greater number of molecules of water than the ions in the crystals, and of this there can be scarcely any doubt.

The number of crystal hydrates for which the values of K_{Cr} have been investigated is very small. These values are compared in Table 7. From them it is clear that for all salt crystal hydrates the value of K_{Cr} is below 75000 atm. (which equals K_1 for water), except for $CaSO_4 \cdot 2H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$. For the latter, the values are not completely trustworthy as the determinations (Raleigh) were carried out from -180° to 0° , and it is therefore possible that the value of $\beta\alpha$ is too low. As for $CaSO_4 \cdot 2H_2O$, it appears that the well-known unusual rapidity of dissolution of the crystals of this salt is also an obvious expression of the fact that the solubility depends on the coarseness of the crystals. That is why, when we consider the low solubility of this salt, we must also accept the fact that this value corresponds to the truth. It is very noteworthy that very low values of K_{Cr} have been obtained for crystals of all acids, in fact, the values are half as great as the value of K_1 for water. A higher value of K_{Cr} has been calculated for $(HPO_3)_n$, metaphosphoric acid, for which we have previously suggested the formula:



this is confirmed 1) by the fact that the density of the vapors even at 800° is twice as great as the theoretical density, 2) by cryoscopic measurements, 3) by the vitreous nature of the acid, and 4) by the preparation of an acid almost

insoluble in water. The usual type of vitreous $(\text{HPO}_3)_n$ is soluble in water, and even deliquesces, but extremely slowly.

Very high values of K_{cr} have been calculated for LiOH , NaOH , and KOH . This forces us to recall that these substances, with a sufficiently small excess of water, form semi-gelatinous, semi-vitreous masses, and that this leads to considerable difficulty when continuous masses of the alkalis are dissolved, and when

T A B L E 7
Intermolecular Linkage of Crystal Hydrates

Substance	C	d	$\beta = 3\alpha$	K_{cr}
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	0.45	1.458	0.03156	17200
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.34	1.78	0.03210	72800
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.34	1.73	0.03362	43000
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	0.372	1.52	0.03110	90000
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	0.345	1.654	0.03650 (0°)	38900
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.273	1.569	0.03107	56000
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	0.354	1.62	0.04801	146000
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	0.374	1.653	0.03263	39000
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.273	2.32	0.0471	186000
H_3BO_3	0.217	1.46	0.04450	370000
HF (-90°)	0.435	0.991	0.0363	14100
HIO_3	0.162	2.8	0.0349	19100
$(\text{HBO}_3)_n$	0.245	1.78	0.0328	32000
H_2SO_4	0.265	1.89	0.0335	23000
H_3PO_4	0.28	1.88	0.0325	26500
NaH_2PO_4	0.272	2.04	0.03039	29000
Na_2HPO_4	0.105	1.53	0.03036	82000
LiOH	0.53	1.4	0.0380	191000
NaOH	0.318	2.02	0.03084	158000
KOH	0.226	2.12	0.03188	52600

they are shipped in iron drums. We must take into account the fact that magnesium oxide has very clearly expressed amphoteric properties which are expressed in the formation of cements (Sorel type), and we would naturally expect that these would also appear in LiOH , which is in some ways close to the alkaline earth subgroup (high melting and boiling points of the metal, very low solubility of Li_2CO_3 , relatively high solubility of LiHCO_3). It would be natural, therefore that if LiOH and NaOH contain very little water, they might show acid properties. In other words some molecules of LiOH (NaOH) would appear to have the structure $\text{H}(\text{LiO})$ and $\text{H}(\text{NaO})$, and therefore, as has been experimentally confirmed upon calcination there takes place a loss of water, which can result only from the reaction:



This also explains the difficulty of removing the last traces of water from almost anhydrous commercial caustic alkali, and it explains the latter's semi-gelatinous form (commercial in the form of rods or chunks). With regard to the decrease in the stability of crystal hydrates, these semi-gelatinous properties must appear more pronouncedly in LiOH than in NaOH and in NaOH than in KOH . In fact, the values of K_{cr} decrease in this order.

It is very possible that in $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ also, the water, although only in part, is of an intercrystalline polyamphion nature, the rest of it being

coordinated water. This, in all probability, also explains the difference between the 17th and 18th molecules of typically intercrystalline polyamphion water, which are easily removed, and the remaining water of hydration and hydrolysis, which is more difficult to remove.

Of late, roentgenographic investigations have shown that only 2 roentgenograms are obtained for gypsum, that is, for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite, while for roasted gypsum a combination of two roentgenograms is obtained. Hence, many authors have concluded that the water of gypsum is zeolite water. But then it remains incomprehensible why the analyses of roasted gypsum always give $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$.

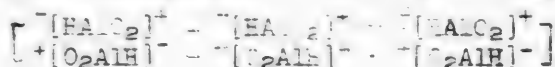
In accordance with what was noted in the paper on the interatomic linkage of silicates and silicoaluminates, these compounds are for the greater part formed not like crystals of salts, which grow by the precipitation and simultaneous dehydration of the ions, but from gels, in which the processes of crystallization take place slowly in the form, so to speak, of an adaptation of individual incipient crystals to others; this is especially characteristic of beryl, with its coordinations of a higher order from hexagons to form tetrahedrons of $[\text{SiO}_4]^{4-}$, $[\text{BeO}]^2+$ and $[\text{AlO}_3]^{3-}$. If we assume that the arrangement and interactions of the oxides of CaO , SO_3 and H_2O are of the same nature in the crystals of gypsum as those of BeO , Al_2O_3 , and Si_2O_4 are in beryl, we arrive at the conclusion that the water does not hydrate any of the ions, but is uniformly distributed among the other oxides, that is, it is not coordinated and not of an intercrystalline polyamphion nature. It does not simply fill a cell in the crystal skeleton, but is attached to it as the groups BeO and Al_2O_3 are attached to the fundamental hexagons of SiO_2 in beryl.

It is self evident that in the nephelites too, although the alkali atoms also fill the cells of the fundamental silica skeleton, without these alkali atoms the silica skeleton would not have the same structure that it does have in nephelite.

Thus, the water in crystal hydrates may be:

a) Water of intercrystalline polyamphions, that is, in excess of the amount which enters into the composition of the hydrate, coordinated ions. Such water, which always exists in $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ in other than the stoichiometric proportion, or the last two (17th and 18th) molecules of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, has a much greater vapor pressure than the rest of the water. Of course, even this excess water is partially coordinated;

b) Water of hydration, that is hydrating water like that which determines the colors of the hydrate vitriols. This is held in different degrees of stability, as in the transition from $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, or as in the case of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which loses its seventh and sixth molecules of water very easily. The loss of the fifth and fourth H_2O from $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ takes place more easily than the loss of the next two. Upon heating, the water from $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ or from the $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ obtained from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ takes with it part of the SO_3 , that is, it is very stably united with the latter, in contrast to the case of gypsum, in which the first molecule of water (upon hydration) or the last (upon dehydration) is lost without any particularly noticeable loss of SO_3 . It is true that part of the latter is lost, but only upon very strong roasting. It is clear that one and a half of the molecules of water are actually bound weakly to the CaSO_4 , while on the other hand the first molecule of water (upon hydration) is bound to the CuSO_4 and especially to the SO_4 very strongly, that is, in all probability it forms a hydroxyl. Finally, in hydrargyllite the water is very stably bound to the Al_2O_3 , forming $\text{Al}(\text{OH})_3$, and in diasore it is still more stable.



There is also a variety of water of hydrolysis, which is found in crystals in the form of H^+ and OH^- , as in K_2SO_4 . These three kinds of water are not sharply differentiated from each other. However, three methods of holding the water do, without doubt, exist. The presence of these three, and the differences between them also explain the ease of solution and the ease of reaction of freshly precipitated oxides such as $Mg(OH)_2$ or of salts, a fact which has long been utilized in analytical chemistry. On the other hand, precipitates which have undergone aging are difficult to dissolve, because of the development of crystallization and the soaking off, or loss, of excess water.

Among the oxides containing water which has been converted into hydroxyl form we may also include $B(OH)_3$, sassolite (370000 atm) which is soluble only when the water is activated by boiling. Among the hydrates with part of the water in purely intercrystalline polyamphion form belong the hydrate $H_2C_2O_4 \cdot 2H_2O$, which has a very low K_{cr} , and $Na_2CO_3 \cdot 10H_2O$ and $CaCl_2 \cdot 6H_2O$, with very low values of K_{cr} . On the other hand, salts with ions of high valence have relatively high values of K_{cr} : $MgCl_2 \cdot 6H_2O$ (56000) on account of the high coordination of Mg, $Na_2HPO_4 \cdot 12H_2O$ on account of the trivalence of PO_4^{---} . It is worth noting that Na_2HPO_4 in which only a single hydroxyl hydrogen remains unsubstituted, $H[HPO_3]OH + 2NaOH \rightleftharpoons 2H(OH) + Na[NaPO_3]OH$, has almost the same K_{cr} both in the anhydrous crystal and in the completely hydrated crystal (82000 and 90000). The singly substituted salt $H[NaPO_3]OH$, which is extremely easy to dehydrate $H[NaPO_3]OH \rightleftharpoons H(OH) + [NaPO_3]$, has a considerably lower value of K_{cr} (one third). The high K_{cr} of $Al_2(SO_4)_3 \cdot 18H_2O$ is the result of the trivalence of the aluminum.

TABLE 8
Intermolecular Linkage of Liquid Salts

	M. p.	C _T	d ₀	β	K ₁	T _{calc.}
KCl	768°	0.168	1.99	0.0 ₃ 36	19000	840°
RbCl	717	0.148	2.76	0.0 ₃ 39	21080	840
TlCl	430	0.0528	7.11	0.0 ₃ 32	24200	550
CuCl	422	0.17	3.53	0.0 ₃ 21	59000	520
HgCl	525	0.0512	7.15	0.0 ₃ 70	11000	550
BeCl ₂	416	0.337	1.90	0.0 ₃ 72	18300	450
MgCl ₂	712	0.233	2.32	0.0 ₃ 17	65600	780
ZnCl ₂	318	0.162	2.92	0.0 ₃ 23	42300	480
SnCl ₂	430	0.102	3.2	0.0 ₃ 36	18700	430
InCl ₃	700	0.189	3.72	0.0 ₃ 20	72400	860
LaCl ₃	800	0.154	3.95	0.0 ₃ 16	78000	950
NaNO ₃	277	0.430	1.91	0.0 ₃ 170	88000	350
KNO ₃	366	0.333	1.90	0.0 ₃ 170	88500	330
AgNO ₃	209	0.240	3.55	0.0 ₃ 175	55400	240

We still have to review the intermolecular linkage of liquid salts, listed in Table 8, and to compare this with the K_{cr} of the same salts in the crystalline condition, listed in Table 9. It can be seen that the values of K_{cr} are from 6 to 2 times as great as the values of K_1 in the case of the halogen compounds, while in the case of the nitrates the differences between K_{cr} and K_1 are not great; for $NaNO_3$ and KNO_3 K_1 is greater than K_{cr} , which is the same phenomenon that has been observed with regard to water and ice.

Thus, we may consider it as demonstrated that for liquid salts, that is, salts whose crystal lattice has been destroyed, the ratio of K_{cr} to K_1 is close to two. In addition there is no doubt that part of the molten salt is coordinated,

that is, the molten salt, like liquid water, is similar to a colloidal solution. Moreover, the transition from the coordinated position (incipient crystallization) to the amorphous surroundings is not sharp, but gradual. On the other hand, there is no doubt that not only crystal hydrate salts, but anhydrous salts with polyvalent ions as well are the coordination limits of the gelatinous condition either as a result of losing their excess water or, in the case of silicates and silicoaluminates, as a result of losing their excess of alkali ions.

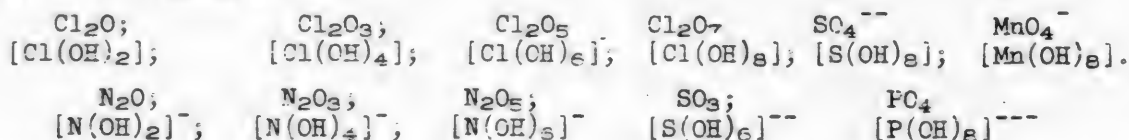
TABLE 9

A Comparison of the Interatomic Linkage of Crystals with the Intermolecular Linkage of Liquids

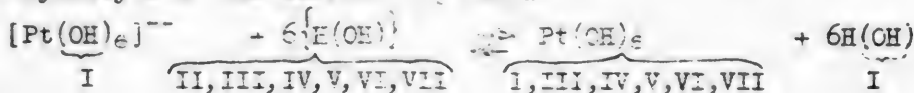
	t	K _l	K _{cr} :K _l	K _{cr}
KCl	840°	19000	3	61000
RbCl	840	26000	2.6	55000
TlCl	500	24000	2.0	48380
CuCl	520	59000	4.4	288000
Hg ₂ Cl ₂	550	11000	6.7	74000
BeCl ₂	450	18000	6.0	116000
MgCl ₂	780	66000	1.9	116000
ZnCl ₂	480	42000	2.3	94000
SnCl ₂	430	19000	2.3	50000 (?)
ICl ₂	860	72000	2.0 (?)	140000 (?)
LaCl ₂	950	78000	2.0	165000
NaNO ₃	350	88000	0.6	56000
KNO ₃	350	88500	0.50	45000
AgNO ₃	240	55400	1.6	59000

Hence we may clearly conclude that between the typical crystal with anhydrous univalent ions having a low coordination tendency (CsCl) and the typical gel (like that of gelatin) there are all degrees of gradual and discontinuous intermediate transitions. On the other hand, from the almost completely non-ionic almost completely dry hexane or liquid methane to a colloidal solution of gelatin, passing through liquids with strongly ionic interchanges and clearly expressed coordinations of the micro particles, there are all fine degrees of discontinuous intermediate transitions.

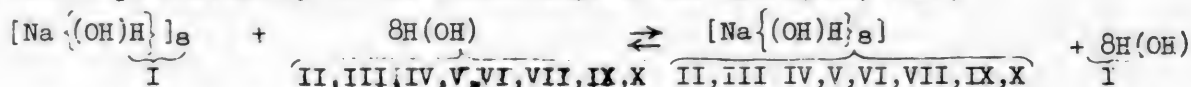
In addition, the very high interatomic linkages of polybasic acids such as H₃PO₃, and without doubt of H₃PO₄ and H₃AlO₃, and even of univalent alkalies, show that water which has added to the oxides, and therefore to the oxygen-containing anion as well, together with the oxygen of the latter, forms a hydroxyl, i.e., that in solution the formula of the acid anions does not fully correspond to [P(OH)₆]⁻⁻⁻, [Al(OH)₆]⁻⁻⁻.



The very attraction into the water is the result of the exchange of the hydrating water (according to the usual nomenclature, or of the hydroxyls coordinated with it, with the hydroxyls of the surrounding water:



It can be understood that with this sort of interchange of attractions, the question of solution is fundamentally decided by the relations of the force of attraction of the hydrated water (or, more accurately, in the case of acid ions, of the hydroxylated water) into the solution, and the attraction toward the hydrated crystal hydrate. Hence we can understand the empirical rule that salts with K_{cr} of the order of 75000 atm are very soluble in water, salts with K_{cr} of the order of 180000 to 260000 atm are very slightly soluble in water, and salts with K_{cr} 300000 atm are insoluble in water. On the other hand, when there is a combination of high-valent ions with low-valent ions, the latter go into the water first, i.e., as if they had been hydrolyzed out of a gel, although the combination, like mica or orthoclase, may be almost completely crystalline. It remains for us to note that hydrated cations like $[Na(OH)H]_s^+$, $[Cu(HO)H]_s^{++}$ are attracted to the water as a result predominantly of the interchange of the hydrogens, i.e.,



Thus we may consider that the coordination hydration of ions, which is the absorption of the coordinately-hydrated ions into the water, is without doubt determined fundamentally by the ionic interchange.

It can be understood that during the solution of univalent ions on the one hand and of high-valent ions on the other, many molecules of $H(OH)$ add on to the first in comparison with the second, and these are added chiefly in the form of hydroxyls as a result of the fundamental interaction during addition. This is the reason why low-valent ions are cations, and only at very high pH become anions (for LiOH, NaOH, KOH, at $pH > 14$), and why the high-valent ions are anions, and only at very low pH are transformed into cations.

SUMMARY

1. K_{cr} for oxygen-containing mono-monovalent salts is of the order of 75000, but is usually lower.
2. K_{cr} for bi-monovalent and mono-bivalent salts is of the order of 100000; in case it is above 150000, the solubility is low.
3. K_{cr} for bi-bivalent salts is 175000. If one of the ions is stably hydrated, the solubility is appreciable.
4. If K_{cr} is above 300000, the substance is insoluble.
5. Spinel, boric acid (sassolite) and vitreous metaphosphoric acid are polyamphion and crystallo-polyamphion compounds, in which the valence of the ions of the polyion is high (3).
6. The ratio between the atomic linkage and the hardness of salts fluctuates within narrow limits.
7. The ratio between the atomic linkage and the melting point of salts fluctuates within relatively narrow limits, both for salts in which the ions are not more than bivalent, and for salts in which there are tri- and quadrivalent ions.
8. Crystals with tri- and quadrivalent ions are limiting coordination gels containing an intercrystalline polyamphion substance in the form of salts with cations of lower valence.
9. The process of solution of oxygen-containing salts consists of at least 1) the hydration of the ions, 2) the swelling of the surface layers, 3) the hydrolysis and breaking off of the lattice and polyion formation, if the ions have a

sufficiently high valence.

10. There is an inverse ratio (approximate) between the hydration of the crystal hydrates, ionically, and their place in the subgroup with regard to inter-atomic linkage and solubility.

11. In crystal hydrates the water exists; a) as intercrystalline polyamphions, b) as water of hydration, c) as water of hydrolysis.

12. K_{cr} for crystal hydrates is of the order of 75000 atm, with some increase in the case of ions of high valence.

13. The crystal hydrates of polyvalent ions have a high K_{cr} as a result of hidden crystalline polyamphion valence.

14. K_{cr} for acids increases as the valence of the ions increases or as crystalline polyamphions are formed ($[HPO_3]_n$ in comparison with H_3PO_4).

15. K_{cr} for alkalies decreases as the coordination valence of their ions decreases.

16. The intermolecular linkage of liquefied salts is of the same order as the K_{cr} of the corresponding crystals.

17. There are all fine degrees of transition between the typical crystal of univalent ions with low coordination ($CsCl$) and typical gels.

18. There are all degree of transition between non-ionic liquid methane and a molten salt (KCl).

19. The anions of oxygen-containing acids are surrounded in solution with hydroxyls.

20. In solution the cations are surrounded chiefly with molecules of water containing hydroxyls oriented in the direction of these cations.

21. The process of drawing hydrated ions into solution takes place as a result of the ionic interchange of the H^+ and OH^- ions of water in the hydrated ions with the water of the solvent.

22. The force of attraction of the hydrated ions into the solution is of the order of K_1 (75000 atm) of water.

23. The reason why cation-forming tendencies prevail in low-valence ions is that only complete molecules of water take part in their coordination.

24. The reason why anion-forming tendencies prevail in polyvalent ions is the presence of numerous hydroxyls which hydrate them; these are produced by the interaction of the oxygens of the anhydrous anion with water and the resultant increase in the hydroxyl concentration of the solution.

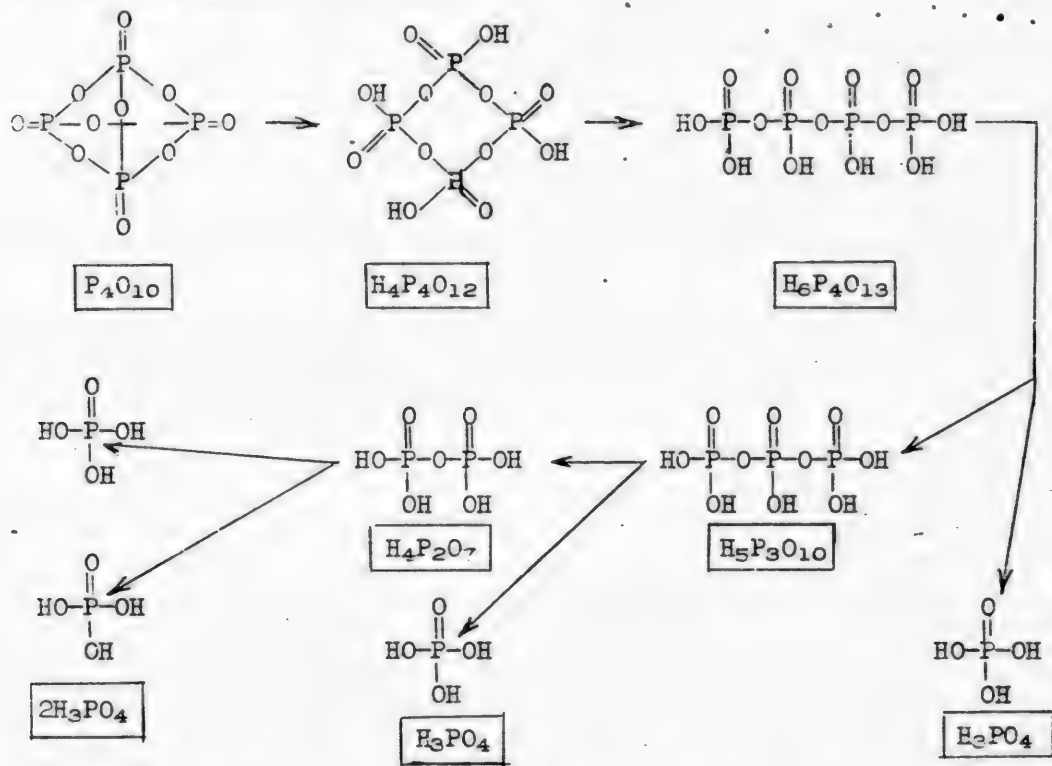
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THE MECHANISM OF HYDRATION OF THE VOLATILE MODIFICATION OF PHOSPHORIC ANHYDRIDE

N I Rodionova and Yu V Khodakov

The objective of the present work was the experimental confirmation of the correctness of the mechanism of hydration of the volatile modification of phosphoric anhydride, previously deduced theoretically by one of the present authors [1].

In accordance with this mechanism, the hydration of P_4O_{10} should take place in the following manner:



Phosphoric anhydride, P_4O_{10} , after passing quickly through the stage of 'disintegration', adds two molecules of water, and is transformed into tetrametaphosphoric acid, $H_4P_4O_{12}$.

Tetrapolyphosphoric acid $H_6P_4O_{13}$ is then formed and this splits off the

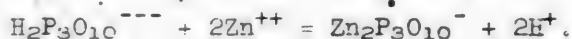
ortho acid to give tripolyphosphoric acid $H_5P_3O_{10}$; the latter splits off H_3PO_4 to give pyrophosphoric acid $H_4P_2O_7$, and the pyro acid finally gives the ortho acid.

Thus, at the initial stage of the process of hydration of P_4O_{10} , in addition to pyrophosphoric acid, tetrapolyphosphoric and tripolyphosphoric acids should be formed. Up to the present time these had not been predicted by any of the investigators who carried out a study of the hydration of phosphoric anhydride.

1 Analytical

In order to investigate the mechanism of hydration, it was first of all necessary to develop a system of analysis which would provide for the determination of tripolyphosphoric acid in addition to the other phosphoric acids, in the presence of tetrameta, ortho, and pyrophosphoric acids. It was first assumed that the direct product of hydration of the metaphosphoric acid theoretically expected (see mechanism), the tetrapolyphosphoric acid, being an unstable substance (it is known that attempts to synthesize its salts have ended unsuccessfully) would not be detected, and therefore, would have no influence on the determination of the tripoly acid.

It was assumed that the method of volumetric determination of the pyro acid of Britske and Dragunov [2] was not specific for pyrophosphoric acid but for the group of acids, and would give only the overall content of polyphosphoric acids. This, in fact, was confirmed: a solution of sodium tripolyphosphate neutral to methyl orange, which contained the tripoly acid in the form of $H_2P_3O_{10}^{---}$ ions, upon addition of a solution of Zn^{++} salts, also neutral, became sharply acid (the methyl orange turned red), although no precipitate was formed (in contradistinction to what happens with pyrophosphate). H^+ ions were liberated as a result of the reaction:



On this fact we based the following method which we worked out for the determination of the tripoly acid (combined with the pyro acid); it is a method using visual means in the acidimetric titration of pyrophosphoric acid, as suggested by Britske and Dragunov: a volume of 5 to 20 ml of the solution of tripolyphosphoric acid or tripolyphosphate is made neutral to methyl orange at a pH 4.2 to 4.4, and 15 to 20 ml of a solution containing a mixture of zinc sulfate and ammonium nitrate (15 g of zinc sulfate and 10 g of ammonium nitrate per 100 ml of water), which has also first been neutralized with methyl orange to a pH of ~ 4 , is added. The resultant solution is titrated with 0.1 N alkali solution to pH 4.2-4.4. During the neutralization and titration MacIlwaine's buffer mixture is used. In view of the fact that the use of the theoretical titre of alkali gives low results for the tripoly acid, the titre must be determined with pure sodium tripolyphosphate. However, for amounts of the tripoly acid no greater than 30 or 40 mg, it is possible in practice to use the theoretical titre, increasing it by 10%.

As this method gives the overall amount of tripoly and pyro phosphoric acids, we also developed a method for the quantitative gravimetric determination of pyrophosphoric acid in the presence of tetrameta, tripoly, and orthophosphoric acids. This permitted us to determine the pyrophosphoric acid in amounts of 3 mg and up.

The method developed can be reduced to the following directions: to 20 to 40 ml of phosphate solution, 10 ml of a 25% solution of zinc acetate is added, then methyl orange is introduced, and 1:1 hydrochloric acid is carefully added until the acidity of the solution is close to pH 3.2. Then a solution of zinc acetate is added until the pH is 3.4 to 3.6, and the solution is allowed to stand for a day. The precipitate of zinc pyrophosphate is filtered off washed with a 0.3% solution of zinc acetate which has been brought to a pH of 3.6 with hydrochloric acid, and toward the end washed twice with cold water. It is then roasted.

As a control to help attain the necessary concentration of hydrogen ions, MacIlwaine's buffer mixture is used.

During the development of this method it was found that tripolyphosphoric acid very greatly slowed down the precipitation of the zinc pyrophosphate, and that if the content of tripoly acid was much higher than that of the pyro acid, in general there was no pyrophosphate precipitate.

A 0.1 N solution of alkali was prepared for the volumetric determinations from chemically pure caustic soda or potash, and the carbonate removed by precipitation with barium nitrate. The excess of barium ions was removed from the solution by the addition of the calculated amount of sodium or potassium sulfate.

The methods of analysis used during the investigation led to the following measurements:

1) The determination of the orthophosphoric acid was carried out by a silver acidimetric titration by Balarev's method, which is based on the precipitation of the HPO_4^{--} ion with an excess of AgNO_3 and the titration of the H_3O^+ ions thus liberated:



2) The determination of the pyrophosphoric acid was carried out according to the directions given above.

3) The determination of the tripolyphosphoric acid was carried out by the volumetric method developed. The tripoly acid was calculated from the amount of alkali used in titration, subtracting the amount used for the pyro acid which had been found.

4) The tetrametaphosphoric acid content was calculated from the difference between the total amount of phosphorus in solution and the amount present in the ortho, tripoly, and pyro acids. The determination of the tetrameta acid was also carried out by using a gravimetric magnesia method on the filtrates after precipitating the other phosphoric acids with silver nitrate at a pH ~8, and then boiling the acidified filtrate in order to transform the meta acid into the ortho acid. This method of determination appeared possible because of the fact that of all the phosphoric acids here mentioned only the tetrametaphosphoric acid was not precipitated by silver salts in contradiction to the data in the literature. Thus, Treadwell and Hall [3] claim that metaphosphoric acid obtained by the solution of phosphoric anhydride in water forms "an additional silver metaphosphate, soluble in ammonia and in mineral acids".

5) As a control, the determination of the ortho acid and of the total of pyro plus tripolyphosphoric acids was also carried out acidimetrically, by the method of Sabatier. The end points (pH) during these titrations were determined by calculation, starting with the corresponding dissociation constants and the measured concentrations of acids which had been found by preliminary titrations.

6) As an indication of the formation of tetrapolyphosphoric acid, which up to the present time had not existed in the perspective of analytical chemistry, the precipitates of silver phosphates formed during the silver acidimetric titration were weighed, and the values obtained were compared with the results obtained by recalculating as silver salts the quantities of ortho, pyro, and tripoly acids which had been found. By comparing these and other results, we confirmed the correctness of the analysis which had been carried out, and testified to the absence of higher polyphosphoric acids. The increased weight of the Ag precipitate in comparison with the weight calculated served to confirm the presence of another acid, in addition to the tetrameta, ortho, pyro, and tripoly phosphoric acids.

As the method of titration, according to Britske and Dragunov, was apparently a group method for all the polyphosphoric acids, a difference between the results obtained for pyrophosphoric acid by the volumetric and gravimetric methods could not serve during the present investigation as a satisfactory index of the formation of the tripolyphosphoric acid. In order to demonstrate the presence of the latter we carried out its precipitation in the form of the difficultly soluble sodium zinc salt. This reaction, which is capable of serving as a qualitative test for the tripoly acid, was carried out in the following manner: during the investigation of hydration in acid medium, after the solution of the anhydride had been allowed to stand at room temperature for 60 to 70 hours, it was neutralized with caustic soda to a pH of 3.5, and to it there was added a concentrated solution of zinc acetate. After 24 hours, the precipitated zinc phosphosphate was filtered off (at this pH, zinc orthophosphate remained in solution), and to the filtrate there was added a saturated solution of sodium chloride. After 2 or 3 days a crystalline precipitate appeared in the solution; microscopic investigation showed this to have the form of prisms.

A chemical analysis of the precipitate, dried at 200°, gave the following results:

Na_2O , 7.8%, ZnO 41.3%, P_2O_5 52.3%.

The composition of the salt, which corresponds to the formula $\text{NaZn}_2\text{P}_3\text{O}_{10}$, should be the following:

Na_2O 7.6%, ZnO 40.0%, P_2O_5 52.4%.

The precipitate, washed with alcohol and ether and dried in the air at room temperature, contained 26.4% of water. Thus, it was determined that the precipitate obtained had the composition $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 8\text{H}_2\text{O}$, which completely corresponded to the data in the literature about tripolyphosphoric acid [4].

The same crystalline precipitate could be separated in a similar manner from a solution of phosphoric anhydride during the investigation of its hydration in alkaline medium.

II. The Preparation of the Original Sample of Phosphoric Anhydride

Commercial phosphoric anhydride, as is known, is not a chemical individual. It is a mixture of a volatile modification of the anhydride (with a molecular lattice) and non-volatile modifications (a coordination lattice).

The volatile modification was obtained by us by sublimation of the commercial sample in a current of dry oxygen in a glass tube at a temperature not higher than 300°.

The sublimed anhydride was transformed into a solution by introducing small portions from a box with vigorous stirring into water which had been cooled to 0°. But this method could not prevent the polymerization of a certain portion of the anhydride as a result of the highly exothermic nature of the reaction, and the formation of some sort of colloidal phosphoric acids in the form of curds. These curds were immediately filtered off.

The hydration of the volatile modification was carried out in acid and alkaline media.

In the first case, the solution of phosphoric anhydride obtained was kept at room temperature, in the second case the solution was immediately made alkaline with the calculated amount of caustic soda, free from carbonates and chlorides, and then heated on a boiling water bath in a closed glass flask.

III. The Hydration of Phosphoric Anhydride in Acid Medium

A solution of the volatile modification of phosphoric anhydride which was used for the investigation was 0.1858 molar in phosphorus (a liter of solution contained 13.19 g of phosphoric anhydride). The molarity of the solution with regard to phosphorus was determined volumetrically, by titration with a solution of alkali, using methyl orange. The temperature of the solution fluctuated during the course of the investigation within the limits 17 to 19°.

For the volumetric determinations, 5 ml of solution was removed with a pipette; for gravimetric determinations of pyrophosphoric acid 5 g or 10 ml was used.

The 0.1 N alkali solution used for titration had a correction factor of 0.9745.

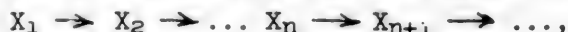
In Table 1 are listed the results obtained; in the curves (Fig. 1) the results given are recalculated to percent of phosphorus present in each of the acids found.

TABLE 1

Total phosphorus content in each test equal to 28.8 mg

Test No.	Time of hydration hrs.	Alkali solution used up in titration, ml.				Increase in weight of $Zn_2P_2O_7$, mg.	Amount of phosphoric acids found, mg.			
		by methyl orange	by phenolphthalein	by Britske-Dragnov	silver acidimetric		tri-poly.	ortho-	pyro-	tetra-meta. by differences
1	0	9.25	9.85	0.45	0.20	none	2.3	0.6	none	25.9
2	25	9.55	10.9	0.95	0.50	traces	4.7	1.5	traces	22.6
3	75	9.55	12.0	1.65	1.0	4.4	6.7	3.0	0.9	18.2
4	120	9.55	12.90	2.05	1.4	9.8	7.0	4.2	2.0	15.6
5	172	9.55	13.70	2.4	1.9	16.0	6.5	5.7	3.2	13.4

In accordance with the theory, we have a chain of consecutive reactions:



each of which is monomolecular in form and is characterized by the velocity:

$$\frac{\partial [X_n]}{\partial t} = K_n [X_n].$$

The decomposition of each molecule of X_n gives rise to a molecule of X_{n+1} , but in addition to the formation of the molecules X_{n+1} , there also takes place their decomposition with the velocity:

$$\frac{\partial [X_{n+1}]}{\partial t} = K_{n+1} [X_{n+1}].$$

Hence the experimentally observed accumulation of the intermediate product X_{n+1} in the solution (Curve $[X_{n+1}] = f(t)$) must be related in a definite way to the change in the concentration of the preceding product X_n (Curve $[X_n] = f(t)$).

After an interval dt , the accumulation of intermediate products is:

$$\Delta [X_{n+1}] = - \partial [X_n] = K_n [X_n] dt;$$

its decomposition:

$$\Delta [X_{n+1}] = K_{n+1} [X_{n+1}] dt,$$

or, to sum up:

$$\frac{\Delta - \Delta'}{dt} = \frac{d[X_{n+1}]}{dt} = K_n[X_n] - K_{n+1}[X_{n+1}].$$

if $K_{n+1} \ll K_n$, then, in accordance with this equation, the curves $[X_{n+1}] = f(t)$ and $X_n = f(t)$ are related to each other as a derivative to its function; in particular, therefore, a point of inflection on the curve $[X_{n+1}] = f(t)$ must correspond to a maximum of the curve $[X_n] = f(t)$.

The results of the investigation show that, during the first stage of the process the hydration of the pyro acid, as was to be expected, is not observed; this is in accord with the theoretical mechanism given above.

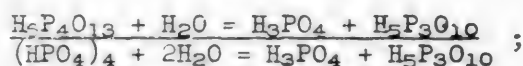
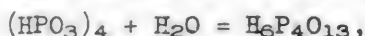
The ratio of the amount of phosphorus in the tripoly acid and the phosphorus in the ortho acid at this stage equals 3:1, i.e.,

$$P_{\text{ortho}} = \frac{1}{3} P_{\text{tripoly}}$$

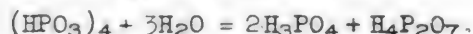
As more and more of the pyro acid is formed, the equation that holds (Table 2) is:

$$P_{\text{ortho}} = \frac{1}{3} P_{\text{tripoly}} + P_{\text{pyro}}$$

This equation is obviously a confirmation of the fact that the process of hydration takes place according to the theoretical mechanism given on page 1401, in accordance with which each molecule of the tetrameta acid, on being hydrated, produces 1 molecule of ortho and 1 molecule of tripoly acid:



for each atom of phosphorus tied up in the ortho acid, the tripoly acid is formed with 3 atoms of phosphorus. Moreover, as a result of the hydration of the tripoly acid, one molecule of the tetrameta acid gives two molecules of ortho and 1 molecule of pyro acid:



For each 2 atoms of phosphorus in the ortho acid, there are 2 atoms of phosphorus in the pyro acid formed.

In order to detect any tetrapolyphosphoric acid, the precipitate of silver phosphates obtained by the silver acidimetric titration was filtered

through a porcelain filter crucible, dried at 130°, and weighed. Although in the first test the weight found was approximately twice as great as the sum of the silver tripolyphosphate and orthophosphate, calculated on the basis of the results obtained in the volumetric determinations, already by the second and the subsequent tests the weight found agreed with that calculated. This fact indicates that during the hydration of the acid solution of the volatile modification of phosphoric

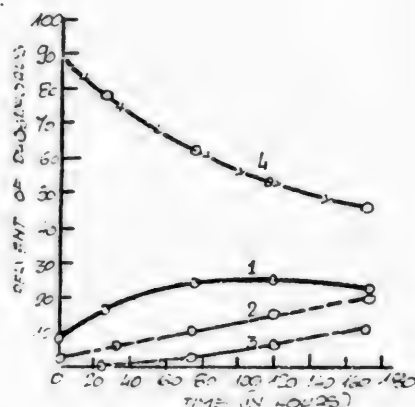


Fig. 1. 1-Tripolyphosphoric acid; 2-Orthophosphoric acid; 3-Pyrophosphoric acid; 4-Metaphosphoric acid

TABLE 2

Test No	$\frac{1}{3}$ tripoly	+ pyro	ortho- (theoret)	ortho- (exptl)
1	$\frac{1}{3}$ 2.3		= 0.8	0.6
2	$\frac{1}{3}$ 4.7		= 1.6	1.5
3	$\frac{1}{3}$ 6.7	+ 0.9	= 3.1	3.0
4	$\frac{1}{3}$ 7.0	+ 2.0	= 4.3	4.2
5	$\frac{1}{3}$ 6.5	+ 3.2	= 5.5	5.7

anhydride no tetrapolyphosphoric acid could be observed.

IV. The Hydration of Phosphoric Anhydride in Alkaline Medium

The investigation was carried out on two solutions.

The first solution was 0.2269 molar in phosphorus (a liter of solution contained 16.11 g of phosphoric anhydride) and 0.57 normal in alkali.

The second solution was 0.2730 molar in phosphorus (a liter of solution contained 19.40 g of phosphoric anhydride) and 0.48 normal in alkali.

The content of phosphorus in the solutions was determined by a gravimetric magnesia method, after transforming the acid into orthophosphoric acid by acidifying the solution with nitric acid and boiling. For volumetric determinations, 3 ml of solution were removed with a pipette, for gravimetric determinations of the pyro acid, 1.5 or 3 ml.

In Tables 3 and 4 are listed the data obtained in the investigation of the first and second solutions. For greater convenience in the comparison of the results of titration with acid and with alkali, the milliliters consumed are recalculated to milliliters of strictly tenth normal solutions.

TABLE 3

Total phosphorus content in each test equals 21.1 mg. Solution I

Test No.	Time of boiling min.	0.1 N solution of alkali used up in titration, ml.		0.1 N solution of acid used up in titration, ml.		Gain in weight of $Zn_2P_2O_7$ mg.	Amounts of phosphoric acids found in mg.		
		by methyl orange	by phenolphthalein	by Britske - Dragunov	silver-acidometric		tri-poly	ortho-	pyro-
1	0	17.2	16.4	0.30	0.10	none	1.5	0.3	none
2	30	17.2	13.95	2.4	1.0	none	12.0	3.1	none
3	60	17.2	13.15	2.9	1.1	none	14.5	3.4	none.
4	180	17.35	12.1	3.1	2.1	about 10	about 12.3	6.5	about 2
5	360	17.4	11.7	3.2	2.4	19.2	10.0	7.4	3.8

TABLE 4

Total phosphorus content in each test equals 25.4 mg. Solution II

Test No.	Time of boiling min.	0.1 N Solution of alkali used up in titration, ml.		0.1 N Solution of acid used up in titration, ml.		Gain in weight of $Zn_2P_2O_7$ mg.	Amounts of phosphoric acids found in mg.		
		by methyl orange	by phenolphthalein	By Britske - Dragunov	silver-acidometric		tri-poly	ortho-	pyro-
1	0	14.5	13.6	0.50	0.15	-	2.5	0.4	-
2	15	14.5	11.75	2.15	0.60	-	10.8	1.9	-
3	45	14.5	10.0	3.1	1.1	-	15.5	3.4	-
4	90	14.55	9.0	3.4	1.8	-	17.0	5.6	-
5	135	14.55	8.5	3.5	2.3	-	17.5	7.1	-
6	180	14.55	8.1	3.8	2.45	10.2	15.5	7.6	2.0

In order to detect any tetrapolyphosphoric acid, the precipitates of silver phosphates obtained by the silver acidimetric titration of the ortho acid were filtered off and weighed in the same way as during the investigation of hydration in acid medium. The content of tetrameta acid was calculated by difference, and was determined in parallel by the gravimetric magnesia method in the filtrates from the silver phosphates. The results obtained for the second solution are listed in Table 5.

TABLE 5

Test No.	Duration of boiling, min	Weight of total silver phosphates, mg		Difference (a - b)	Gain in weight of $Mg_2P_2O_7$, mg	Amount of tetrameta acid (in mg phosphorus)		Difference (d - c)
		Found (a)	Calculated (b)			Found (c)	Calculated (d)	
1	0	52	27	25	66.1	18.4	22.5	4.1
2	15	135	117	18	34.8	9.7	12.7	3.0
3	45	198	178	20	12.2	3.4	6.5	3.1
4	90	229	220	9	4.3	1.2	2.8	1.6
5	135	244	245	- 1	3.0	0.8	0.6	0.0
6	180	252	254	- 2	2.2	0.6	0.3	- 0.3

The data of Tables 3, 4, and 5, recalculated to percent of phosphorus, are given in the general graph (Fig. 2), insofar as, despite some difference in the composition of the first and second solutions, the points on the graph corresponding to them lie on one and the same curve.

The results of the experiments carried out on the process of hydration show that under the conditions described for the experiments, the hydration of phosphoric acid takes place more quickly in alkaline solution than in acid.

In alkaline medium, as in acid, no pyro acid is formed during the first stage of hydration. The pyro acid can be observed with complete certainty only 3 hours after the beginning of hydration. However, when we take into account the interference of the considerable amounts of tripoly acid on the precipitation of the zinc pyrophosphate, in connection with the course of the curve for the formation of the pyro acid (Fig. 2), apparently considerable amounts of the latter are already formed even from 1.5 to 2 hours after the beginning of hydration.

While the curves $[H_3PO_4] = f(t)$ and $[H_2P_2O_7] = f(t)$ in alkaline medium differ little in nature from the corresponding curves for hydration in acid medium, the curve $[H_5P_3O_{10}] = f(t)$ in alkaline medium has a higher and a more sharply expressed maximum. The amount of phosphorus in the tripoly acid before the formation of the pyro acid begins exceeds the amount of phosphorus in the ortho acid not by a factor of 3, as it should according to the theory but is from 4 to 6 times as great. However, further on, with the appearance of the pyro acid, the equation which holds is:

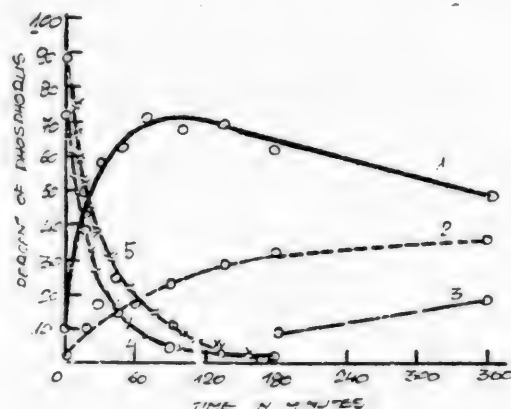


Fig. 2. 1-Tripolyphosphoric acid; 2-orthophosphoric acid; 3-pyrophosphoric acid; 4-meta, found; 5-meta, calculated

$$P_{\text{ortho-}} = \frac{1}{3} P_{\text{tripoly-}} + P_{\text{pyro-}}$$

The concentration of tetrameta acid calculated by difference, during the first stage of hydration in alkaline medium exceeds the amount of tetrameta acid found.

All these results, which differ from those obtained during the investigation of hydration in acid medium, as well as the fact that the amount of silver phosphates found in the first stage exceed the calculated amount (1st, 2nd, 3rd, and 4th tests, Table 5) point to the fact that during the first stage of hydration in alkaline medium some sort of polyphosphoric acid is formed (in addition to the pyro and tripoly acid), which is titrated by the Britske-Dragunov method, and forms a difficultly soluble silver salt.

If we assume that during hydration in alkaline medium tripolyphosphoric acid is formed during the first stage of the process in amounts which correspond to the ratio:

$$P_{\text{tripoly-}} = 3(P_{\text{ortho-}} - P_{\text{pyro-}}),$$

and take into account the amounts of unhydrated tetrameta acid found (Table 5), then we can calculate the amount of phosphorus which goes into this polyacid for the second solution of the alkaline hydration.

These calculations for 15, 45, and 90 minutes of elapsed hydration (2nd, 3rd, and 4th tests) are listed in Table 6. (In view of the small amounts of solution used in the titration of the first test, and the considerable relative errors which result in the determination because of this, the results of the first test are disregarded in these calculations).

TABLE 6

Acid	15 minutes		45 minutes		90 minutes	
	Found, % P	Calculated % P	Found, % P	Calculated, % P	Found, % P	Calculated, % P
Meta, found ..	38.2	-	13.4	-	4.7	-
Meta, decomposed	-	61.8	-	86.6	-	95.3
Ortho-	7.5	-	13.4	-	22.0	-
Tripoly-	-	22.5 (= 7.5 x 3)	-	40.2 (= 13.4 x 3)	-	5 (= (22-3) x 3)
Pyro-	-	-	-	-	-	3
Remaining phosphorus ..	-	31.8 (= 61.8 - 7.5 - 22.5)	-	33 (= 86.6 - 13.4 - 40.2)	-	13.3 (= 95.3 - 22 - 57 - 3)

In accordance with the theory, the unknown acid formed under the conditions of alkaline hydration is the tetrapoly acid, and the last line of Table 6 thus expresses the content of this acid in percent of the amount of phosphorus going into it. We can verify this statement by calculating the theoretical total weight of silver precipitates under the assumption that "remaining phosphorus" is the tetrapoly acid, and comparing the results of the calculation with the experimental data of Table 5.

Table 7 shows that the weight of silver precipitates theoretically calculated in this manner agrees with the experimental value.

The hydration of the volatile modification of phosphoric anhydride in

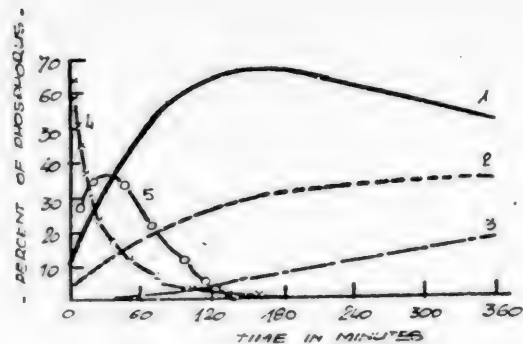


Fig. 3. 1-Tripolyphosphoric acid; 2-orthophosphoric acid; 3-pyrophosphoric acid; 4-metaphosphoric acid; 5-tetrapolyphosphoric acid.

TABLE 7.

Test No	Duration of boiling in min.	Weight of total silver phosphates, mg.		Difference, (a - b)
		Found (a)	Calculated, (b)	
2	15	135	138	-3
3	45	198	199	-1
4	90	229	233	-4

alkaline medium (0.25 molar with regard to phosphorus and 0.5 N with regard to alkali) at 100°, on the basis of Tables 3, 4, 5, and 6, may be thus presented graphically (Fig. 3).

With regard to the theoretical mechanism given on page 1403:

1) The first product of hydration to be observed, the metaphosphoric acid, decomposes according to an experimental curve for a reaction of the first order.

2) The direct product of hydration of the meta acid is, without doubt, tetrapolyphosphoric acid; this is clear from the fact that $\frac{[H_5P_4O_{13}]}{\partial t}$ from the very beginning doubtless has its final value, and that in the rising part of the curve $[H_5P_4O_{13}] = f(t)$ there is no point of inflection;

3) The tripoly acid is not formed directly from the meta acid, but is the direct decomposition product of the tetrapolyphosphoric acid; this is clear from the fact that the rising part of the curve $[H_5P_3O_{10}] = f(t)$ has a point of inflection, corresponding to the time for the maximum of the curve, $[H_5P_4O_{13}] = f(t)$; i.e., the velocity of formation of new $H_5P_3O_{10}$ is greatest exactly when the hydration product from which it is formed, the $H_5P_4O_{13}$, reaches its highest concentration.

4) The pyro acid, following the $H_5P_3O_{10}$ genetically as a product of hydration, appears in the hydrating solution after all the other acids.

5) The curve $[H_3PO_4] = f(t)$ does not express an equation for a reaction of the first order; in the first stage of the process, when the H_3PO_4 is formed chiefly because of the relatively rapid hydration of $H_5P_4O_{13}$, the velocity constant for the accumulation of H_3PO_4 is relatively great, but in the second stage when the H_3PO_4 is formed chiefly because of the slower splitting off from $H_5P_3O_{10}$, it is relatively small.

A sufficiently thorough comparison of the theory with experiment in all details permits us to confirm the fact that the problem of the mechanism of hydration of the volatile modification of phosphoric acid has been solved.

SUMMARY

1. It has been shown experimentally that all the previously proposed mechanisms for the hydration of phosphoric anhydride and all the experimental investigations of this process are inadequate, as they do not take into account the participation in the process of the higher polyphosphoric acids as intermediate products; these are the tetrapoly acid $H_5P_4O_{13}$ and the tripoly acid $H_5P_3O_{10}$.

2. It has been shown experimentally that the process of hydration of the volatile modification of phosphoric anhydride P_2O_5 both in acid and in alkaline

medium takes place corresponding to the mechanism which has been deduced from the theory of structure of anhydrides and higher phosphoric acids, proposed by one of the authors (see page 1401).

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THE PHYSICO CHEMICAL INVESTIGATION OF IODINE SOLUTIONS

VII. THE SYSTEM NICKEL HEXAMMINO IODIDE- IODINE

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The polyhalides now known may be divided into four groups according to the number of halogen atoms attached to a single equivalent of cation: tri, penta, hepta, and nona polyhalides.

In the series of inorganic polyhalides with simple (non-complex) cations, representatives of only the lowest of these groups are known. There are few references in the literature to the isolation from solution, and moreover in unsolvated condition, of such polyhalides as KI_7 , CsI_7 , and CsI_9 ; it is impossible to consider them as substantiated, and they can justifiably be disputed.

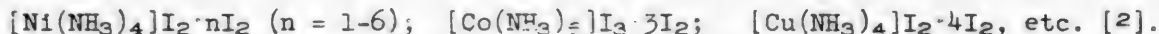
These facts can be explained on the basis of the hypothesis that polarization plays a part in the mechanism of formation of compounds of the polyhalide type and in the factors determining their stability. This is in close relation to the polarizability of the coordinated halogen molecules and to the counter-polarization effect, which makes its appearance in this connection in the cations of polyhalides.

The most stable of the polyhalides are therefore the polyiodides, whose cations have a large ionic radius and an inert-gas electron shell, and therefore have a very weak polarizing action. The polyiodides of cesium, for example, are of this type.

The higher, the hepta and nona, polyhalides, are known for a few organic halides whose complex cations are characterized by a large ionic radius. Examples are the polyiodides of the tetra-substituted ammonium bases:



In connection with these facts, the production and investigation of inorganic polyhalides with complex cations is of interest. Such compounds are as yet known only in very small number. They are mostly the polyiodides of the amines of a few metals (Ni, Co, Cu, Zn, Cd), obtained from aqueous solutions by Ephraïm and Moosmann:



To compounds of this type we can also refer the carbamides of trivalent metals (Fe, Co, Al), such as $[Al(CO_2NH_2)_3]I_3 \cdot 3I_2$ [3,4].

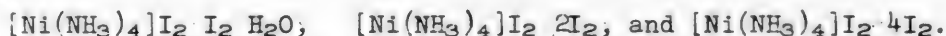
Starting from the considerations indicated above about the factors of

stability of the polyhalides, we undertook an investigation of solutions of the iodides of complex amino compounds in liquid iodine by the methods of physico-chemical analysis.

In the present communication, there is a description of the results of the investigation of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - Iodine.

We were chiefly interested in the question of what were the compounds richest in iodine that could be formed in this system.

Polyiodides of nickel tetrammino compounds were obtained by Ephraim and Mosimann by the action of an aqueous solution of iodine on an aqueous solution of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ or on a solution of NiCl_2 and ammonia. Polyiodides of different compositions precipitated out of the solution, depending on the molar ratio of amino compound and iodine. If for 1 mole of nickel amino compound there were 1, 2, and 4 moles of iodine, the polyiodides formed were of the respective compositions:



If 8 moles of iodine were used per 1 mole of amino compound, part of the iodine remained in solution and formed a product whose composition was close only to that of a heptapolyiodide $[\text{Ni}(\text{NH}_3)_4]\text{I}_2 \cdot 6\text{I}_2$.

Upon reviewing these experimental data, our attention was drawn to the fact that even in those cases where nickel hexammino chloride was used as the starting material, the polyiodides of the nickel tetrammino compound were obtained. Ephraim and Mosimann do not explain the cause of this phenomenon.

In the opinion of Ephraim and Mosimann, these four polyiodides of nickel amino compounds correspond to far from sharply defined members of a series of compounds. Depending on the amount of iodine used, different amounts of it are added, not always corresponding to the total number of atoms, to give a continuous series of iodine-containing solid solutions.

In connection with these results, we decided to investigate the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine by the method of thermal analysis. In addition, we decided to study this system in its electrochemical aspects as well - to determine the electrical conductivity and the nature of the electrolyte, and to compare it in this respect with others of the previously studied iodine - iodide systems [5,6] which were like it.

EXPERIMENTAL

The hexammino iodide of nickel was obtained by the following method [2].

NiCO_3 was dissolved in hydriodic acid. The excess of acid was first neutralized with a solution of ammonia, and then a large excess of the latter was added. The precipitate which formed during this, of the difficultly soluble (in the cold) $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ was then recrystallized from a hot aqueous solution, washed first with a concentrated solution of ammonia, then with alcohol and a mixture of alcohol and ether (1:1) and dried at 60-70°.

The compound was obtained in the form of a violet-blue finely crystalline powder.

Chemical analysis of the compound obtained confirmed the fact that it was pure $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$.

The iodine was purified in the manner described in preceding communications. After numerous sublimations and drying, the melting point of the iodine was 113.4° and its electrical conductivity was $1.78 \cdot 10^{-5} - 2 \cdot 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 130°. This indicated the high degree of purity of the preparation.

a) Thermal analysis

In order to determine the crystallization temperatures of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine, we used the vessel described in the work of Fialkov and Kuzmenko [8] for the thermal analysis of the systems iodine - potassium, rubidium, and thallium iodides. The procedure of the experiment is also described there.

The temperature was measured after every 30 seconds or 1 minute with a thermometer containing divisions of 0.1° . First we determined the hardening temperature of the molten iodine, and then we introduced a sample of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ into the vessel, increasing its concentration gradually. In order to make sure that the iodide dissolved, the vessel was first maintained in an air thermostat (with periodic shaking) at such a temperature that the reaction mass was in a molten condition. The crystallization temperature was then determined. The experiment with each sample was repeated 2 or 3 times, until constant values were obtained, with variations which did not exceed a few tenths of a degree.

At higher concentrations of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, the color of the hardened melt changed from a metallic gray for pure iodine to a reddish-brown.

By the method of thermal analysis we were able to investigate the system only up to a concentration of 21 Mol. % $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, at which the limit of the solubility of the nickel hexammino iodide was reached in molten iodine under the conditions of the experiment.

We carried out four series of measurements, the results of which are listed in Table 1.

TABLE 1
Thermal analysis of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine

Molar percent of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$	Arrest point		Molar percent of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$	Arrest point	
	First	Second		First	Second
4.5	104.1	79.4	11.2	95.8	-
6.0	99.4	85.8	11.5	96.6	-
7.0	95.3	86.4	13.0	-	94.2
8.0	89.2	86.4	13.9	117.0	94.3
8.5	-	86.4	15.1	-	93.2
8.9	-	85.5	16.0	131.9	94.3
9.0	-	86.4	17.0	133.5	-
9.5	93.3	86.3	18.0	135.5	93.0
10.0	96.5	86.3	18.8	135.4	93.5
10.5	97.0	-	21.3	133.4	-
11.0	97.5	-			

On the melting point diagram of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine (Fig. 1), two eutectics can be seen with 9.0 and 12.8 mol % of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, and melting points 86.4 and 94.3° , as well as a dystectic with 11.1 mol % of nickel hexammino iodide corresponding to the nonapolyiodide $[\text{Ni}(\text{NH}_3)_6]\text{I}_{2.8}\text{I}_2$.

A second dystectic indicated at close to 20 mol % of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, is referred to the pentapolyiodide. Investigation of this system at high concentrations was already impossible as a result of reaching the limit of solubility of the $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ in the molten iodine.

Thus, the results of thermal analysis made it possible to observe the first representative of the inorganic nonapolyiodides $[\text{Ni}(\text{NH}_3)_6](\text{I}_2)_n$.

Nickel hexammino nona-polyiodide, obtained by melting together stoichiometric amounts of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ and iodine, is a finely crystalline substance with a dark gray color. It is decomposed by water with the evolution of bubbles of gas. The solution is colored red-brown. Upon treatment with ether it is partially decomposed, giving up part of its iodine; there remains a product whose composition is close to that of the triiodide.

b) The Electrical Conductivity of the System

$[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine

The measurements of electrical conductivity were carried out in a flask of the form which has been described in the work of Plotnikov, Fialkov, and Chaly [5].

The electrical conductivity was measured at 130 and 140° in a thermostat with petroleum oil. The fluctuation of the temperature during the period of the experiments did not exceed 0.3°. The minimum of sound for pure iodine was somewhat dull and diffused, for melts of all concentrations it was very clear.

In each series of experiments, the electrical conductivity of the molten iodine was first determined, and then the electrical conductivity of solutions of continuously increasing concentrations of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ in iodine. These solutions were prepared directly in the vessel for the measurement of electrical conductivity. The vessel with the melt was first maintained for some time at the temperature selected (for complete solution of the sample of iodide) and the electrical conductivity was then measured. The experiment was repeated 2 or 3 times, until a constant value of the electrical conductivity was obtained.

The results of the measurements are listed in Table 2.

The system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine has a great electrical conductivity even at low concentrations of the iodide. Even at a concentration of 0.22 mol.% of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, the electrical conductivity of the melt is almost 50 times as high as the electrical conductivity of the molten iodine.

As the concentration of the $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ increases the specific electrical conductivity at first increases sharply, and even at only 3.5 mol.% reaches a value of the order of $0.1 \text{ ohm}^{-1} \text{ cm}^{-1}$. Upon further increasing the concentration of the nickel hexammino iodide, the increase of the specific electrical conductivity is slowed down. After reaching a value of $2 \cdot 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$, the specific electrical conductivity remains constant.

The value of the electrical conductivity, and the appearance of the isotherm of specific electrical conductivity of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine are very close to those of iodine solutions of KI , RbI , and $[(\text{CH}_3)_4\text{N}]\text{I}$.

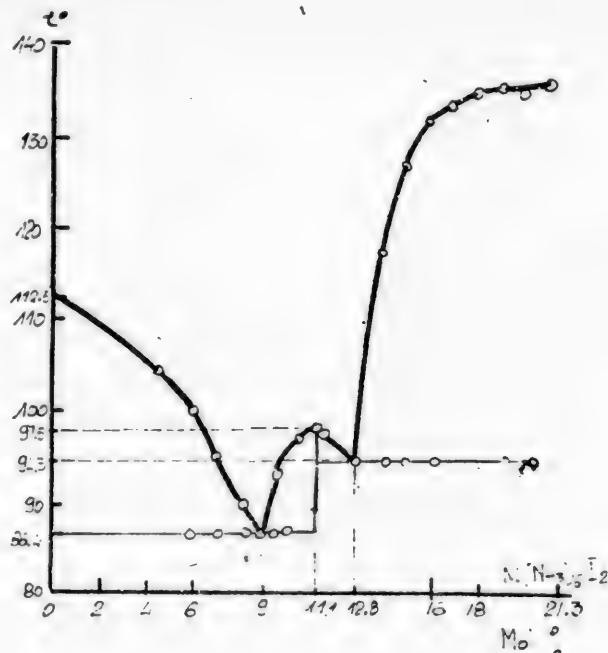


Fig. 1. Melting point diagram of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine.

TABLE 2

Electrical conductivity of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine

Molar percent of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$	Specific electrical conductivity		Dilution, ml	Molecular electric- al conductivity at 130°
	130°	140°		
0	$1.78 \cdot 10^{-5}$	$1.40 \cdot 10^{-5}$	-	-
0.22	$1.04 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	28928	30.1
0.56	$5.19 \cdot 10^{-3}$	$5.27 \cdot 10^{-3}$	11408	59.2
0.81	$9.60 \cdot 10^{-3}$	$9.62 \cdot 10^{-3}$	8141	78.2
1.28	$2.38 \cdot 10^{-2}$	$2.47 \cdot 10^{-2}$	5133	122.2
2.03	$5.22 \cdot 10^{-2}$	$5.44 \cdot 10^{-2}$	3287	171.6
2.17	$5.51 \cdot 10^{-2}$	$5.61 \cdot 10^{-2}$	3069	169.1
3.02	$9.73 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	2238	217.8
4.30	$1.49 \cdot 10^{-1}$	$1.55 \cdot 10^{-1}$	1601	238.5
6.27	$1.86 \cdot 10^{-1}$	$2.03 \cdot 10^{-1}$	1129	209.9
8.23	$1.99 \cdot 10^{-1}$	$2.03 \cdot 10^{-1}$	884.7	176.1
9.08	$2.13 \cdot 10^{-1}$	$2.16 \cdot 10^{-1}$	813.0	173.2
12.62	$2.13 \cdot 10^{-1}$	$2.18 \cdot 10^{-1}$	615.5	131.3
12.81	$2.12 \cdot 10^{-1}$	-	507.1	128.7

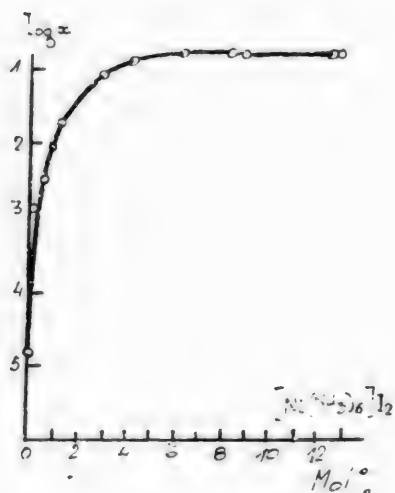


Fig. 2. Isotherm of specific electrical conductivity.

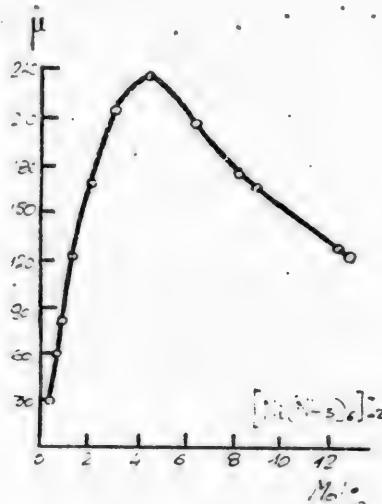


Fig. 3. Isotherm of molecular electrical conductivity.

However the temperature coefficient of the electrical conductivity of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine has a positive value even in the region of very low concentrations of iodide, while for the other iodide solutions just cited the temperature coefficient of electrical conductivity is first negative, and acquires a positive value at higher concentrations of the iodides.

The isotherms of molecular electrical conductivity of KI , RbI , $[(\text{CH}_3)_4\text{N}]\text{I}$ and $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ carry the analogy further. The isotherms of electrical conductivity of these systems may be referred to the type of anomalous curves. With an increase in the concentration of iodides the molecular electrical conductivity quickly increases, reaches a maximum value, and then falls. The isotherms of

specific and molecular electrical conductivity are given in Figs. 2 and 3.

The specific gravity of the solutions of nickel hexammino iodide in molten iodine was determined at 130° in a pycnometer with a graduated neck [6]. The values of the specific gravity are shown in Table 3.

T A B L E 3

Specific gravity of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine at 130°

Molar percent of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$	d_{20}^{130}
0	3.9174
1.07	3.881
3.93	3.8063
5.93	3.7460
10.42	3.5962

In order to decide the question of the nature of the electrolyte in the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine, it was necessary to make clear the molecular composition of the nickel hexammino iodide in the iodine solution.

With this purpose we carried out cryoscopic measurements of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine. For our calculations of the molecular weight we utilized the values of the cryoscopic constant for iodine determined by Beckmann [9] and equal to 204 (calculated for 100 g of iodine). The results of the measurements of the values of the molecular weight of the nickel hexammino iodide are listed in Table 4.

T A B L E 4

Cryoscopy of the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine
Mol. weight of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2 = 414.7$; mol. weight of $[\text{Ni}(\text{NH}_3)_6](\text{I}_3)_2 = 2445$

Weight of iodine, g	Weight of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, g	Molar percent	Δt	M_1	M_2
69.0310	0.3660	0.32	0.56	191.4	1169
	0.6114	0.54	0.70	258.1	1591
	0.9026	0.79	0.80	333.4	2100
	1.1704	1.03	0.84	411.8	2648
	1.4599	1.28	0.86	501.7	3300
	1.7307	1.51	1.16	440.9	2964
	1.9978	1.74	1.55	380.0	2617
	2.3081	2.00	2.02	337.6	2381
	2.8786	2.88	2.88	295.3	2188

Just as in the work of Fialkov and Akselrud [8], we calculated the molecular weight on the basis of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ as the dissolved substance, with M_1 , and also on the basis of the polyiodide $[\text{Ni}(\text{NH}_3)_6](\text{I}_3)_2$, with M_2 .

The molecular weight of the nickel hexammino iodide, as well as of the nonapolyiodide in the region of low concentrations was considerably less than that corresponding to the formula. With an increase in the concentration of the iodide it first increased, became greater than the value corresponding to the formula then began to decrease.

A similar change of the value of the molecular weight with the concentration of iodide, as calculated from the cryoscopic data, had also been observed in the system $(\text{CH}_3)_4\text{Ni}$ - iodine [8].

We must point out that the decrease of the apparent association factor with an increase in the concentration of iodides has also been observed in cryoscopic measurements of the excellently current-conducting iodine solutions of alkali metals [9] and of thallium iodide [10].

A comparison of these data with the increase in electrical conductivity observed in both these systems during the increase in the concentration of iodides (Table 2 and Fig. 2) leads to the following conclusion about the nature of the electrolyte in the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine: at low concentrations of the iodide, the current-conducting particles are products of the electrolytic dissociation of the monomeric molecules of the polyiodides (or also of the molecules of $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$). As the concentration of the iodide in the iodine solution is increased, the molecules of polyiodide are associated, as a result of which their molecular weight begins to increase, and becomes greater than the theoretical value. But during all this, the electrical conductivity of the system not only does not decrease, but continues to increase.

Similar results about the increase in electrical conductivity during the simultaneous increase in the degree of association of complex molecules have often been observed in investigation of anhydrous solutions [11,12]. A great number of such results have been described in researches of the Inst. of Gen. and Inorg. Chem. of the Acad. Sci. USSR [13,14].

This relationship of the process of association of the molecules of the polyiodides and their electrolytic dissociation in iodine solutions is bound up with the increase in the concentration of iodides, and again leads to a decrease in the apparent molecular weight as determined by the cryoscopic method.

S U M M A R Y

1. The formation of polyiodides in the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine has been shown by the method of thermal analysis. The nonapolyiodide $[\text{Ni}(\text{NH}_3)_6](\text{I}_9)_2$ has been detected on the melting point diagram of this system.

2. The results of thermal analysis, electrical conductivity measurements, cryoscopic measurements, and a comparison of the results obtained with the data in the literature lead us to conclude that the electrolyte in the system $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ - iodine consists of both monomeric and associated molecules of the nonapolyiodide $[\text{Ni}(\text{NH}_3)_6](\text{I}_9)_2$.

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And also in the system $(\text{CH}_3)_4\text{NI}$ -iodine..

AN INVESTIGATION OF THE TERNARY SYSTEM OF CALCIUM, POTASSIUM AND SODIUM NITRATES IN MELTS

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An investigation of the melting point diagrams of the ternary system of calcium, potassium and sodium nitrates forms part of our investigation of mutual quaternary systems of nitrates and nitrites of these metals.

In the system, the surface of the liquidus was investigated by a visual-polythermic method of physico-chemical analysis. The melting point diagram of this system was first studied by Menzies and Dutt [1], who determined a ternary eutectic point at 175° and the composition: 33% mol. equiv. of calcium nitrate, 51.9% mol. equiv. of sodium nitrate, and 15.1% mol. equiv. of potassium nitrate. The electrical conductivity of the salt melts of this system was investigated by E.R.Natsvlishvili and A.G.Bergman, and the specific gravity and viscosity of the ternary system of sodium, potassium, and calcium nitrates was studied by A.G.Bergman, together with N.E.Schmidt and I.S.Rassonsky. The isodensity diagrams by the above-named authors had the character of smooth curves running almost parallel to the side sodium nitrate - potassium nitrate; they indicated a considerable increase of the specific gravity when the concentration of calcium nitrate in the salt melt was increased.

The isoviscosity diagrams at the same temperatures as the isodensity diagrams showed a sharp increase in viscosity with an increase in the content of calcium nitrate.

Binary Systems

1. The binary system potassium nitrate - sodium nitrate has been studied by many authors: Hissinc [2], Brisco and Madgin [3], A.G.Bergman and N.M.Veksberg [4] and others.

The study of this system which we repeated gave results in good agreement with the results of the two preceding authors. The results of the experimental investigations are listed in Table 1 and Fig. 1.

The binary system potassium nitrate - sodium nitrate is a good illustration of the dependence of the form of the curve for cooling or heating on the velocity of cooling. This fact explains, as A.G.Bergman has shown [4], the discrepancies with the results of Hissinc [2]. On the heating curves, definite eutectic pauses are to be observed in a fairly broad interval, in which the cooling curves do not have any. Therefore, if we construct a composition - property diagram on the basis of the cooling curves, we obtain a diagram which illustrates the formation of a continuous series of solid solutions, with a minimum. The diagram obtained from the form of the heating curves shows the formation of solid solutions with limited solubility on two sides. The more slowly the heating and cooling are

TABLE 1

Binary system: sodium nitrate - potassium nitrate

Point No.	Percent mol. equiv.		Temp. first crystals	Point No.	Percent mol. equiv.		Temp. of first crystals
	NaNO ₃	KNO ₃			NaNO ₃	KNO ₃	
1	100	0	337°	15	50	50	222°
2	97.5	2.5	328	16	45	55	225
3	95	5	324	17	40	60	229
4	92.5	7.5	316	18	35	65	237
5	90	10	310	19	30	70	245
6	87.5	12.5	306	20	25	75	257
7	85	15	297	21	22.5	77.5	262
8	82.5	17.5	290	22	20	80	266
9	80	20	282	23	17.5	82.5	273
10	75	25	270	24	15	85	276
11	70	30	257	25	12.5	87.5	283
12	65	35	243	26	10	90	286
13	60	40	231	27	5	95	300
14	55	45	226	28	0	100	308

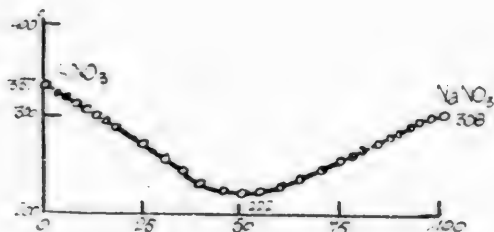


Fig. 1

carried out, the more closely do these two types of diagrams fuse into one.

The formation of a continuous series of solid solutions of potassium and sodium nitrates can be explained by the well known fact that solid solutions obtained in cases where the substances have identical or similar crystalline structures, with cells of almost the same dimensions, not very different at atomic or ionic radii, and melting points close to each other. We have all the enumerated properties, as comparison

shows, for the nitrates of potassium and sodium.

2. The binary system sodium nitrate - calcium nitrate has been studied by Menzies and Dutt [1], who gave a melting point diagram with a eutectic at 236.5° and the composition: 33.3 mol. equiv. of sodium nitrate and 66.7% mol. equiv. of calcium nitrate.

A three-fold repeated investigation of this system, carried out by us, confirmed the general character of the diagram, but gave other data: the eutectic point corresponded to a temperature of 232° and a composition of 54.1% mol. equiv. of sodium nitrate and 45.9% mol. equiv. of calcium nitrate (Table 2, Fig. 2).

The liquidus curve had two branches of crystallization: a calcium nitrate branch steeply descending down to the eutectic point and a smooth branch rising almost in a straight line for the sodium nitrate. The branch for the crystallization of the calcium nitrate could be followed from the ordinate with the composition: 80% mol. equiv. Ca(NO₃)₂ and 20% mol. equiv. (NaNO₃)₂, which melted at 454°; above this temperature, decomposition of the salts began.

3. The binary system potassium nitrate - calcium nitrate was studied by Menzies

TABLE 2

Point No.	Percent mol. equiv.		Temp. first crystals	Point No.	Percent mol. equiv.		Temp. first crystals
	$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$			$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$	
1	80	20	454°	13	45	55	236°
2	75	25	424	14	43	57	240
3	70	30	394	15	40	60	245
4	65	35	365	16	35	65	253
5	63	37	347	17	30	70	263
6	60	40	330	18	25	75	271
7	58	42	312	19	20	80	278
8	55	45	292	20	15	85	287
9	53	47	278	21	10	90	294
10	50	50	257	22	5	95	303
11	48	52	240	23	0	100	308
12	45.9	54.1	232				

and Dutt [1], as already cited and by Prof. A.P. Rostkovsky [5]. The first authors gave a melting point diagram with a eutectic at 210.5° and a composition of 75% mol. equiv. of calcium nitrate and 25% mol. equiv. of potassium nitrate. The investigations of A.P. Rostkovsky led to other results. He found a double incongruent compound: $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$, which melted with decomposition at 174°, with a eutectic at 145°. The transition point corresponded to the composition 55.5% mol. equiv. of potassium nitrate and 44.5% mol. equiv. of calcium nitrate. The ordinate of the compound: 33.3% mol. $\text{Ca}(\text{NO}_3)_2$ and 66.7% mol. $(\text{KNO}_3)_2$ was determined by A.P. Rostkovsky by means of the heating and cooling curves. In addition, he studied the micrograms of the melts of different parts of the diagram, and was able to observe needle-shaped crystals of the compound cited above. Numerous repeated measurements of the melting points of melts of this binary system confirmed the conclusions of A. P. Rostkovsky and the nature of the melting point diagram. A eutectic point of the same composition was obtained at 146°.

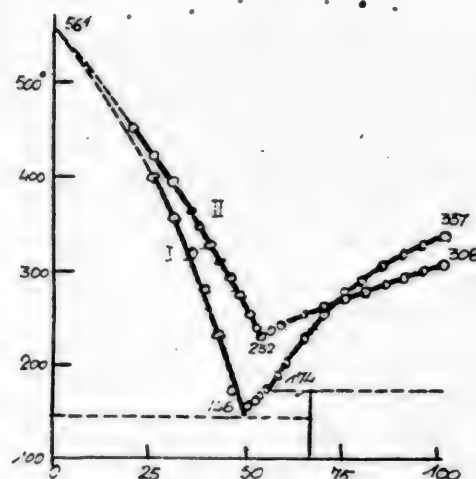


Fig. 2.

I- $\text{Ca}(\text{NO}_3)_2 \rightarrow (\text{KNO}_3)_2$ II- $\text{Ca}(\text{NO}_3)_2 \rightarrow (\text{NaNO}_3)_2$.

The liquidus curve had three branches of crystallization (Fig. 2, Table 3). There was a calcium nitrate branch, dropping sharply down to the eutectic point; a very short branch of the incongruous compound, rising from the eutectic to the transition point at 174°, and a steeply rising branch for the crystallization of the potassium nitrate. The branch for the crystallization of the calcium nitrate could be followed to the ordinate of 75% mol. equiv composition in calcium nitrate, above 403°, decomposition began (in Fig. 2 this is shown by the dotted lines).

A study of this system presented considerable experimental difficulties. As a result of the great viscosity of the salt melts, the velocity of the formation

TABLE 3

Point No.	Percent mol. equiv.		Temp. first crystals	Point No.	Percent mol. equiv.		Temp. first crystals
	$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$			$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$	
1	75	25	403°	13	45	55	174°
2	70	30	357	14	42.5	57.5	192
3	65	35	321	15	40	60	204
4	62.5	37.5	283	16	35	65	230
5	60	40	260	17	30	70	257
6	57.5	42.5	236	18	25	75	277
7	55	45	208	19	20	80	297
8	52.5	47.5	171	20	15	85	309
9	51	49	146	21	10	90	320
10	50	50	153	22	5	95	329
11	49	51	157	23	0	100	337
12	48	52	165				

and growth of crystals was considerably slowed up, and in consequence supercooling of the melt took place, and the temperature at which the first crystals were formed in the middle of the diagram was from 40 to 80° too low. The introduction of primers, and energetic rubbing of the walls of the tube with a stirrer did not always produce the desired results, and therefore some points were determined by the disappearance of the crystals, during very slow and careful heating.

When the melts containing from 40 to 55% mol. equiv. of $(\text{KNO}_3)_2$ were cooled to room temperature a transparent vitreous mass was obtained with a high coefficient of expansion. Test tubes which were allowed to stand with the hardened glass cracked, but the transparent colorless glass, which was stable at room temperature, was easily devitrified by the action of the moisture of the air.

Ternary Sections

In order to study the interaction of sodium, potassium, and calcium nitrates in melts, and to make clear the nature of the space melting point diagrams, eight cross-sections were made. From the calcium nitrate - potassium nitrate side of the triangle, sections I, II, and III were made toward the $(\text{NaNO}_3)_2$ corner; from the calcium nitrate - sodium nitrate side, section IV, V, VI, VII, and VIII were made. Their nature and distribution are shown in Fig. 3.

TABLE 4

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	$(\text{NaNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$			$(\text{NaNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$	
1	0	40	60	204°	7	30	28	42	184°
2	5	38	57	185	8	35	26	39	195
3	10	36	54	172	9	40	24	36	207
4	15	34	51	165	10	50	20	30	230
5	20	32	48	160	11	60	16	24	249
6	25	30	45	170	12	70	12	18	263

Cross-section I. 40% $\text{Ca}(\text{NO}_3)_2$ + 60% $(\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)$ has two branches of crystallization: a slightly concave potassium nitrate branch, and a convex, open rising calcium nitrate branch. The transition point corresponds to a temperature of 160° and a composition: 20% mol. equiv. $(\text{NaNO}_3)_2$, 48% mol. equiv. $(\text{KNO}_3)_2$, and 32% mol.

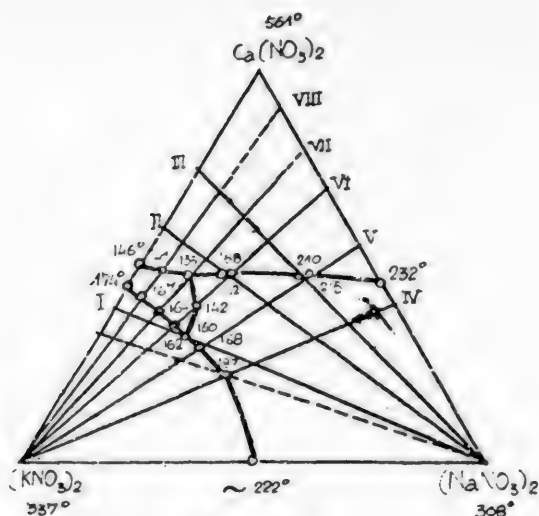


Fig. 3.

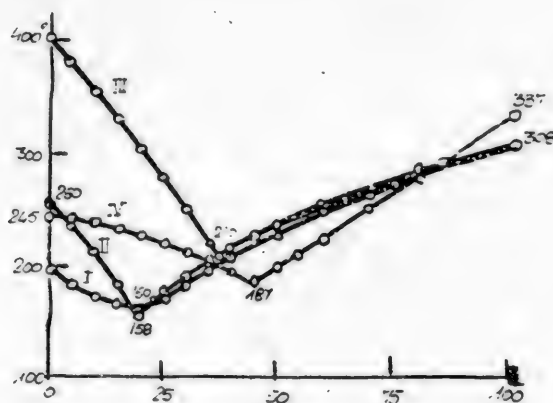


Fig. 4.

- I-40% $\text{Ca}(\text{NO}_3)_2$ + 60% $(\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$
 II-60% $\text{Ca}(\text{NO}_3)_2$ + 40% $(\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$
 III-75% $\text{Ca}(\text{NO}_3)_2$ + 25% $(\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$
 IV-40% $\text{Ca}(\text{NO}_3)_2$ + 60% $(\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$

equiv. $\text{Ca}(\text{NO}_3)_2$ (Fig. 4 and Table 4).

No vitrification was observed over the entire extent of the liquid curve of this section. Along the branch for the crystallization of the potassium nitrate, between the ordinates of composition 15 to 20% sodium nitrate the melt that formed had a viscous consistency which made the process of crystallization and the determination of the appearance of the first and the disappearance of the last crystals more difficult.

Section II. 60% $\text{Ca}(\text{NO}_3)_2$ + 40% $(\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$ had two branches of crystallization: a steeply descending branch of calcium nitrate and an open, rising branch for the crystallization of the sodium nitrate.

The transition point corresponded to a temperature of 158° and the composition: 20% mol. equiv. $(\text{NaNO}_3)_2$, 48% mol. equiv. $\text{Ca}(\text{NO}_3)_2$, and 32% mol. equiv. $(\text{KNO}_3)_2$ (Fig. 4, Table 5).

TABLE 5

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	$(\text{NaNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$			$(\text{NaNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$	
1	0	60	40	260°	8	30	42	28	211°
2	5	57	38	238	9	35	39	26	202
3	10	54	36	212	10	40	36	24	216
4	15	51	34	182	11	50	30	20	235
5	20	48	32	158	12	60	24	16	252
6	23	46	31	168	13	75	15	10	278
7	25	45	30	176	14	85	9	6	293

Along the branch for the crystallization of the calcium nitrate between the ordinates of composition 13 to 17% mol. equiv. sodium nitrate, glass formation was observed; this made the process of crystallization very difficult.

As more and more sodium nitrate was added, the tendency towards supercooling

decreased, and further along the branch of the liquidus, the crystallization of sodium nitrate took place normally.

Section III. $75\% \text{Ca(NO}_3)_2 + 25\% (\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$ had two branches of crystallization: a branch for the crystallization of calcium nitrate, dropping steeply to the transition point, and a branch for the crystallization of sodium nitrate, rising smoothly from the transition point.

The transition point corresponded to a temperature of 210° and a composition: 37 % mol. equiv. sodium nitrate, 47% mol. equiv. calcium nitrate, and 16% mol. equiv. potassium nitrate (Fig. 4, Table 6).

TABLE 6

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	$(\text{NaNO}_3)_2$	$\text{Ca(NO}_3)_2$	$(\text{KNO}_3)_2$			$(\text{NaNO}_3)_2$	$\text{Ca(NO}_3)_2$	$(\text{KNO}_3)_2$	
1	0	75	25	404°	9	37	47	16	210°
2	5	71	24	380	10	40	45	15	218
3	10	67.5	22.5	355	11	45	41	14	229
4	15	63.5	21.5	331	12	50	37	13	240
5	20	60	20	304	13	60	30	10	255
6	25	56	19	281	14	70	22	8	273
7	30	52	18	251	15	80	15	5	287
8	35	48.5	16.5	221					

Along the line of this section no glass formation was observed. Along the branch for the crystallization of the calcium nitrate, between the ordinates of composition from 10 to 30% mol. equiv. sodium nitrate there was a tendency to supercooling, which disappeared as the concentration of sodium nitrate was increased.

Section IV. $40\% \text{Ca(NO}_3)_2 + 60\% (\text{KNO}_3)_2 \rightarrow (\text{NaNO}_3)_2$ had two branches of crystallization: a branch for the crystallization of sodium nitrate, descending smoothly to the transition point, and a branch for the potassium nitrate, rising in a straight line from the transition point.

The transition point corresponded to a temperature of 187° and the composition: 45% mol. equiv. potassium nitrate, 22% mol. equiv. calcium nitrate and 33% mol. equiv. sodium nitrate. Along the lines of this cross section, no glass formation was observed, and crystallization took place normally. (Fig. 4, Table 7).

TABLE 7

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	$(\text{NaNO}_3)_2$	$\text{Ca(NO}_3)_2$	$(\text{KNO}_3)_2$			$(\text{NaNO}_3)_2$	$\text{Ca(NO}_3)_2$	$(\text{KNO}_3)_2$	
1	0	40	60	245°	9	40	24	36	195°
2	5	38	57	243	10	45	22	33	187
3	10	36	54	239	11	50	20	30	202
4	15	34	51	233	12	55	18	27	212
5	20	32	48	229	13	60	16	24	227
6	25	30	45	220	14	70	12	18	251
7	30	28	42	214	15	80	10	10	280
8	35	26	39	205					

The object of sections I and IV was to determine the spot where the line of simultaneous crystallization was crossed, separating the regions of crystallization of sodium and potassium nitrates.

The object of sections II and III was to determine the spot where the line of simultaneous crystallization was crossed, separating the regions of crystallization of calcium and sodium nitrates.

Section V. $55\% \text{Ca}(\text{NO}_3)_2 + 45\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$ had three branches of crystallization: a calcium nitrate branch, dropping steeply down to the transition point 215° ; a sodium nitrate branch, dropping smoothly from the point 215° to the second transition point 168° ; and a branch for the crystallization of potassium nitrate rising steeply from the second transition point (Fig. 5, Table 8).

TABLE 8

Pt. No.	Percent mol. equiv			Temp. first crystals	Pt. No.	Per cent mol. equiv.			Temp. first crystals
	$(\text{KNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$			$(\text{KNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$	
1	0	55	45	294°	11	40	33	27	178°
2	5	52	43	284	12	45	30	25	170
3	10	49	41	258	13	46	29.5	24.5	168
4	11.5	48.5	40	240	14	50	27	23	183
5	12.5	48	39.5	215	15	55	24.5	20.5	202
6	15	46.5	38.5	212	16	60	22	18	220
7	20	44	36	208	17	65	19	16	235
8	25	41	34	201	18	70	16.5	13.5	251
9	30	38	32	195	19	75	14	11	265
10	35	35.5	29.5	185	20	85	8	7	297

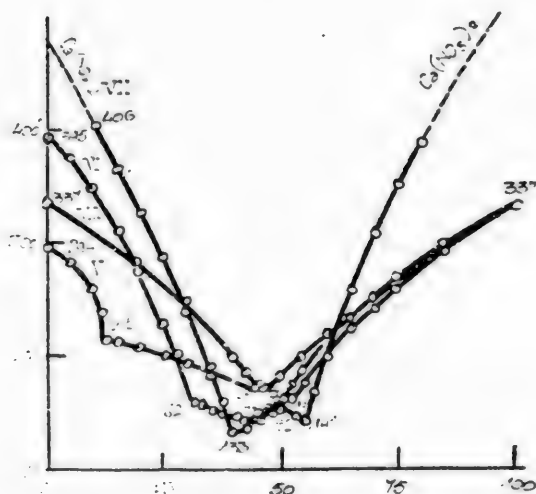


Fig. 5.

V-55% $\text{Ca}(\text{NO}_3)_2 + 45\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$
 VI-70% $\text{Ca}(\text{NO}_3)_2 + 30\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$
 VII-80% $\text{Ca}(\text{NO}_3)_2 + 20\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$
 VIII-90% $\text{Ca}(\text{NO}_3)_2 + 10\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$

Section V has two transition points: the first corresponds to a temperature of 215° and the composition: 12.5% mol. equiv. potassium nitrate, 48% mol. equiv. calcium nitrate, and 39.5% mol. equiv. sodium nitrate; the second to 168° and the composition: 46% mol. equiv. potassium nitrate, 29.5% mol. equiv. calcium nitrate and 24.5% mol. equiv. sodium nitrate. No glass-formation was observed along the line of this cross section, and the salt crystallized normally.

Section VI. $70\% \text{Ca}(\text{NO}_3)_2 + 30\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$ had four branches of crystallization: a branch for the crystallization of calcium nitrate, dropping steeply down to the transition point at 162° ; a branch for the crystallization of sodium nitrate dropping directly from the transition point 162° to the transition point 142° ; a branch for the crystallization of the incongruent compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$, rising smoothly from

the transition point 142.5° to the transition point 162.5° ; and a branch for the crystallization of potassium nitrate, rising steeply from the transition point 162.5° .

Section VI had three transition points, which corresponded to the temperatures and compositions: 1) 162° and 31.5% mol. equiv. potassium nitrate, 48% mol. equiv. calcium nitrate, and 20.5% mol. equiv. sodium nitrate; 2) 142° and 42.5% mol. equiv. potassium nitrate, 40% mol. equiv. calcium nitrate, and 17.5% mol. equiv. sodium nitrate; 3) 162.5° and 50% mol. equiv. potassium nitrate, 35% mol. equiv. calcium nitrate, and 15% mol. equiv. sodium nitrate (Fig. 5, Table 9).

TABLE 9

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	(KNO ₃) ₂	Ca(NO ₃) ₂	(NaNO ₃) ₂			(KNO ₃) ₂	Ca(NO ₃) ₂	(NaNO ₃) ₂	
1	0	70	30	395°	13	40	42	18	147°
2	5	66.5	28.5	376	14	42.5	40	17.5	142
3	10	63	27	349	15	45	38.5	16.5	147
4	15	59.5	27.5	312	16	47.5	37	15.5	154
5	20	56	24	273	17	50	35	15	162.5
6	25	52.5	22.5	230	18	52.5	33	14.5	175
7	27.5	52	21.5	202	19	55	31	14	187
8	30	49	21	180	20	60	28	12	212
9	31.5	48	20.5	162	21	65	24.5	10.5	234
10	32.5	47.5	20	158	22	70	21	9	252
11	35	45.5	19.5	155	23	75	17.5	7.5	269
12	37.5	43.5	19.0	151	24	80	14	6	300

Along the line of this cross-section, between the coordinates of composition 20 to 55% mol. equiv, there was glass-formation which made the process of crystallization extremely difficult. In the upper part of the melting point diagram of Section VI, the salt melts crystallized comparatively normally.

Section VII: 20% (NaNO₃)₂ + 80% Ca(NO₃)₂ → (KNO₃)₂ had three branches of crystallization: a calcium nitrate branch very steeply dropping to 133° ; a branch for the incongruent compound 4KNO₃ · Ca(NO₃)₂, rising smoothly to 164° , and a potassium nitrate branch, slightly convex, and rising steeply to 164° .

TABLE 10

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. no.	Percent mol. equiv.			Temp. first crystals
	(KNO ₃) ₂	Ca(NO ₃) ₂	(NaNO ₃) ₂			(KNO ₃) ₂	Ca(NO ₃) ₂	(NaNO ₃) ₂	
1	10	72	18	406°	10	45	44	11	144°
2	15	68	17	367	11	47.5	42	10.5	150
3	20	64	16	328	12	50	40	10	157
4	25	60	15	287	13	51.5	38.7	9.8	164
5	30	56	14	242	14	55	36	9	178
6	35	52	13	189	15	60	32	8	205
7	37.5	50	12.5	160	16	65	28	7	224
8	39.4	48.8	11.8	133	17	70	24	6	244
9	42.5	46	11.5	138	18	75	20	5	260

Section VII had two transition points. The first transition point corresponded to the temperature 133° and the composition: 39.4% mol. equiv. potassium nitrate 48.8% mol. equiv. calcium nitrate and 11.8% mol. equiv. sodium nitrate.

This was a ternary eutectic point. The second had the temperature 164° and the composition: 51.5% mol. equiv. potassium nitrate, 38.7% mol. equiv. calcium nitrate, and 9.8% mol. equiv. sodium nitrate. Along the line for section VII between the ordinates for the composition from 33 to 45% mol. equiv. potassium nitrate, glass formation took place, making the process of crystallization more difficult (Fig. 5 Table 10).

Section VIII. $80\% (\text{KNO}_3)_2 + 18\% \text{Ca}(\text{NO}_3)_2 + 2\% (\text{NaNO}_3)_2 \rightarrow (\text{KNO}_3)_2$, had three branches of crystallization: a calcium nitrate branch, dropping sharply to 141° ; a branch for the incongruent compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$, rising in a straight line from the point 141° to the transition point 167° ; and a potassium nitrate branch, rising steeply from the transition point.

Section VIII had two transition points. The first corresponded to a temperature of 141° and the composition: 55% mol. equiv. potassium nitrate 40.2% mol. equiv. calcium nitrate, and 4.8% mol. equiv. sodium nitrate; the second, a temperature of 167° and the composition: 48% mol. equiv. of potassium nitrate, 46.6% mol. equiv. of calcium nitrate and 5.4% mol. equiv. of sodium nitrate. Along the line of cross-section VIII between the ordinates of composition 40 to 55% mol. equiv. potassium nitrate, glass formation was observed (Fig. 5, Table 11).

TABLE 11

Pt. No.	Percent mol. equiv.			Temp. first crystals	Pt. No.	Percent mol. equiv.			Temp. first crystals
	$(\text{KNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$			$(\text{KNO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	$(\text{NaNO}_3)_2$	
1	80	18	2	371°	10	48	46.6	5.4	167°
2	75	22.5	2.5	352	11	47	47.5	5.5	168
3	70	27	3	310	12	45	49.2	5.8	173
4	65	31.2	3.8	258	13	43	51	6	186
5	60	38.5	4.2	202	14	40	53.7	6.3	200
6	57.5	38	4.5	171	15	30	63	7	248
7	55	40.2	4.8	141	16	20	72	8	283
8	53	22	5	148	17	0	90	10	337
9	50	44.8	5.2	157					

Along the line of cross-section VII the melting points of the salts were measured up to 400° , while along the line of cross-section VIII they were measured to 390° . Above these points, the decomposition of the salts was observed.

The results of the experimental investigation of the ternary system of the nitrates of calcium, potassium, and sodium are summarized in a projection of the triangular isotherms of the spatial diagram of state (Fig. 6).

The isotherms are given for 25° intervals. The isotherms from 425° and higher were obtained by extrapolation, and are dotted lines.

The composition at the invariant and transition points was found experimentally and checked by an orthogonal

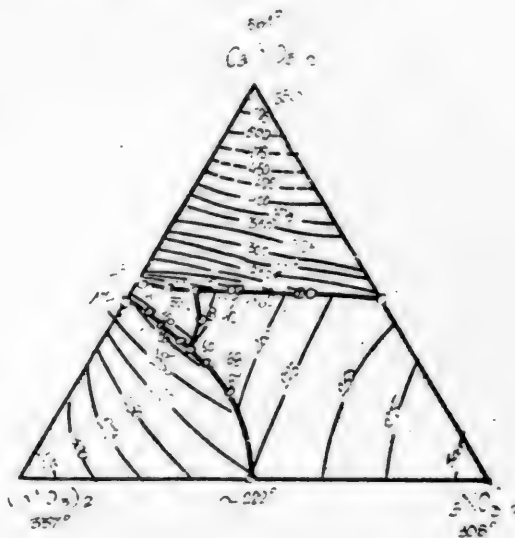


Fig. 6.

projection of the curves of simultaneous crystallization along the side of the triangle corresponding to sodium nitrate - potassium nitrate (Fig. 7).

Characteristic peculiarities of crystallization were observed on this projection:

1) The curve for the simultaneous crystallization of sodium nitrate - calcium nitrate, like the curve for the simultaneous formation of the compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$ and KNO_3 had a normal convexity to the axis of composition.

2) The curve for the simultaneous crystallization of NaNO_3 and KNO_3 had a concave form, characteristic for solid solutions. It was also worth noting that the lowest melting component, NaNO_3 (308°) had the greatest region of crystallization, the area of crystallization of this compound being 42.5%, while the areas of crystallization of the remaining compounds were. $\text{Ca}(\text{NO}_3)_2$ 28.1%, KNO_3 26.6%, and $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$ 2.8%.

The tininess of the area of crystallization of the compound confirms its lack of stability. A description of the binary systems and of the inner sections of the triangle (cross-sections) permits us to note the difference between the properties and behavior of sodium and potassium nitrates in the melts, during their interaction with calcium nitrate.

1. The melting point diagram of the binary system: potassium nitrate - calcium nitrate has a transition point which indicates the formation of the incongruent compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$ with a eutectic point at 146° , i.e., 86° below the first, although the melting point of potassium nitrate is 29° higher than the melting point of sodium nitrate. The lowering of the eutectic point must be regarded as the result of the formation of a chemical compound. At the same time, as has already been noted more than once, there is glass formation both in the binary and in the ternary cross-sections of the components at low concentrations of sodium nitrate.

2. The melting point diagram of the binary system: sodium nitrate - calcium nitrate has a simple eutectic at 232° , without the formation of a vitreous mass.

The formation of the low-melting nitrate glasses of the simplest composition in the system potassium nitrate - calcium nitrate and in the ternary system of calcium, potassium, and sodium nitrates has been determined for the first time. This fact is without doubt of great interest. It is necessary to note that in nitrate systems with a greater tendency to form glass, potassium and calcium ions are present. This follows from the binary systems described above, and is confirmed by sections II, IV, VI, and VIII. The region of glass formation is considerably greater than the area of crystallization of the incongruent compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$, and is approximately sketched out by the 175° isothermal lines. This is a region with great concentrations of potassium and calcium nitrates and low concentrations of sodium nitrate (Fig. 6).

Thus, the question of the substitution of the sodium nitrate by a more accessible salt in the charge for a salt bath has found a practical solution. The economy of substituting calcium nitrate for sodium nitrate is obvious, when we consider the possibility of obtaining calcium nitrate industrially by neutralizing nitrous gases with milk of lime.

SUMMARY

1. The ternary system of calcium, potassium, and sodium nitrates has been investigated by a visual-polythermal method.



Fig. 7.

2. The field of crystallization of the binary incongruent compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$ has been shown, thus confirming the conclusions of A.P. Rostkovsky, drawn by him on the basis of a study of the binary system potassium nitrate - calcium nitrate.

3. It has been found, contrary to the results of Menzies and Dutt, that the ternary system of calcium, potassium, and sodium nitrates may be referred to the systems with two invariant points:

a) A ternary eutectic point at 133° and the composition: 39.4% mol. equiv. potassium nitrate, 48.8% mol. equiv. calcium nitrate, and 11.8% mol. equiv. sodium nitrate;

b) a ternary transition point at 160° and the composition: 49.2% mol. equiv. potassium nitrate, 32.8% mol. equiv. calcium nitrate, and 18% mol. equiv. sodium nitrate.

The present work has been carried out in the laboratory of the department of general and inorganic chemistry of the V.M. Molotov Rostov-on-Don State University.

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ON THE AUTOACTIVATION OF ZINC SULFIDE

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As is well known, the preparation of the blue phosphorescent zinc sulfide first described by Schloede [1] is in contradiction to the classical experiments of Lenard and Tomashek. According to Lenard, the method of testing the sulfide for purity consists of roasting it with a flux. If the powder obtained after roasting does not phosphoresce upon excitation with ultraviolet, the sulfide is sufficiently pure.

Zinc sulfide with a blue phosphorescence was also obtained upon roasting with a flux, and at the present time, after the investigations of Riehl [2] and Rothschild [3], no doubt arises about the purity of the original sulfide and in the reproducibility of the results of the experiment. It is known that the previous history of the zinc sulfide, used by Tomashek differed from that of Schleede in this way: the former was precipitated with hydrogen sulfide from an ammoniacal medium, and the second from an acid medium [4,5]. The sulfides obtained were strikingly different in appearance. that obtained from the ammoniacal medium was very fine, precipitated badly, and became very lumpy upon drying; that obtained from acid medium was in the form of fairly large grains, precipitated well, and upon drying formed a dusty, very mobile powder. Insofar as the zinc sulfides obtained differed only in these respects, the difference in luminescent properties must be sought in the factors preceding the precipitation of the sulfide.

In order to explain this contradiction, we set up the following experiments. Zinc sulfide, obtained by precipitation from acid medium and free from heavy metals (the iron content was less than $10^{-5}\%$, that of copper less than $10^{-6}\%$) was mixed with a solution of pure sodium sulfide that did not contain heavy metals, heated and washed to remove sulfates. The easily precipitated sulfide, after standing in contact with the solution of sodium sulfide, was transformed into a suspension that was very difficult to clarify, and this settled badly when washed, even when the wash waters contained only traces of sodium sulfide. The zinc sulfide thus obtained was dried, mixed with sodium chloride, which was used as a flux, and roasted at 850° . The sulfide obtained after calcination did not luminesce at all. Sulfide which had been roasted in the same way, but not treated with sodium sulfide, luminesced with a clear blue light.

In order to determine the reversibility of the process, the following experiment was carried out. Zinc sulfide, obtained by precipitation from sulfuric acid, was treated with sodium sulfide and washed in the manner described. The treated sulfide was separated into two portions. One portion was dried and used as a charge with sodium chloride, while the second was added to a 5% solution of sulfuric acid, heated, washed three times with water, dried, and used as a charge with sodium chloride. Both portions were roasted at 850° for 1 hour, as a result of which the first sulfide was obtained in a non-luminescent condition as before, while the second was obtained in luminescent condition, completely identical with the control sample.

This experiment demonstrated the reversibility of the process which was responsible for the appearance of the blue luminescence of zinc sulfide, and as we confirmed, could be repeated any number of times if the necessary precautions were taken against accidental contamination, especially during washing.

Completely analogous results were obtained when ammonium sulfide was used in place of sodium sulfide. Only the process of reversion became slower as a result.

The next point to be verified in the experiments described by Tomashek was the investigation of the activity of extraneous activators. For this purpose we used copper. It is known that when negligible traces of copper are introduced ($\sim 10^{-6}$ g Cu per 1 g ZnS) into the sulfide, obtained by precipitation from acid, a condition of blue-green fluorescence is obtained after roasting. This has two maxima of illumination: one at 460-470 m μ , corresponding to the radiation of the unactivated luminophore, and the other at 510-520 m μ , corresponding to the radiation of the copper.

It appeared that when negligible traces of copper (10^{-6} g Cu per 1 g ZnS) were introduced into the zinc sulfide, roasting with a flux gave a green luminescence with one radiation maximum corresponding to that of the copper. This confirmed the results of Tomashek, who calcinated non-luminescent zinc sulfide with an activator and a flux to obtain the luminescent sulfide.

We verified the sensitiveness of the reaction of the non-luminescent sulfide to copper and showed that appreciable radiation was caused by the copper even in a concentration of $10^{-6}\%$, so that the method described can serve as a control for the copper content of precipitated zinc sulfide.

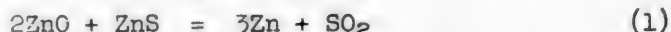
All the experiments mentioned above were also carried out with cadmium sulfide. In this case the charge was prepared by using a mixture of treated cadmium sulfide with treated zinc sulfide (ZnS 70%, CdS 30%) in order that the illumination might be located in the visible region of the spectrum. All the rules found for zinc sulfide were confirmed for the case of cadmium sulfide as well.

Although the experiments described above showed clearly that the lack of agreement in the experimental facts existing in the literature was only apparent, they still did not give any explanation of the phenomenon. The radiation of the blue zinc sulfide has been explained by a number of authors [1,2,3,6] as the auto-activation of the zinc sulfide by the excess of zinc atoms, and if this is actually so, then our experiments must give the conditions for the "precipitation" of these excess zinc atoms (or cadmium atoms). Both in the case of the sulfide obtained by precipitation from acid medium and in that of the sulfide precipitated from an ammoniacal medium or treated with alkaline sulfide, we were dealing fundamentally with zinc sulfide. The only difference was that in the first case it was contaminated by the adsorption of acid anions which could oxidize upon drying to give zinc sulfate in some, possibly very slight, amount. In the standard method used for the preparation of zinc sulfide from acid media [4,5], the precipitation is carried out in sulfuric acid medium, and the sulfide obtained always contains a few tenths of a percent of sulfate. In the second case the zinc sulfide carries an adsorbed layer of sulfide ions which hinder oxidation during drying and there is doubtless a fair amount of contamination with alkali sulfide because of the difficulty of washing it off. Thus, from the chemical point of view the difference leads, apparently, in the first case to the presence of zinc oxide or an oxygen-containing zinc salt which is transformed into the oxide at high temperature. At high temperature, zinc oxide can be a source of metallic zinc by two methods. In the first place, it is known [7] that at high temperature zinc oxide turns into a luminophore, whose capacity to emit light is related to a trifling excess of zinc. From the data on dissociation pressure, however, it follows that at a temperature of 1000°K the decomposition of zinc oxide to give metallic zinc and

oxygen is negligible. The velocity of this process has not been studied to a great extent, but the period of roasting of the sulfide is not great, and from the thermodynamic data it is impossible to draw sufficiently well-founded conclusions, inasmuch as they refer to equilibrium systems.

The second method of formation of metallic zinc from zinc oxide and sulfide is analogous to the well-known process of the blackening of zinc sulfide in light.

It is known that the blackening of the sulfide takes place only in the presence of moisture [8]. This, apparently, signifies that the zinc sulfide itself does not decompose, but that the decomposition takes place only after its partial oxidation. Oxidation gives zinc oxide or sulfate, which can react with zinc sulfide according to the equation:



or



Curie [8] has shown the possibility of reaction (1). It is thermodynamically possible, but its kinetics have not yet been measured.

Other explanations for the formation of metallic zinc are improbable. For example, the dissociation of zinc sulfide according to the equation



is possible, but is improbable even at high temperatures, and in reality scarcely takes place, as it would lead to the luminescent condition even in the second case, in the absence of oxygen-containing compounds of zinc.

The dissociation of the zinc chloride obtained in the synthesis of lumino-phores [5] is very small at its boiling point, and the formation of atomic zinc as the result of this dissociation is very improbable. Moreover, if this were responsible for the autoactivity of the sulfide, the luminescent condition would be obtained both in the case of the sulfide containing an oxidized layer and of the sulfide with an excess of sulfide ion. Thus, we may conclude that the process of autoactivation of the zinc sulfide is analogous to a certain extent to photochemical blackening, and is explained by the course of the reaction between zinc oxide or an oxygen-containing salt of zinc and zinc sulfide, with the formation of sulfur dioxide and atomic zinc.

The case is different for the activation of zinc sulfide with copper. As follows from our experiments, and also from the classical work of Lenard and Tomashek, activation by copper takes place both in the presence of oxygen compounds and in their absence. This clearly indicates that the chemical mechanism for the production of activation is here different.

Of all the possible methods of obtaining atomic copper, we may consider the following three:



The dissociation pressure of reactions (4) and (5) is negligibly small at the temperature of roasting. At the same time, if we can assume in the case of zinc sulfide that it is sufficient for only a small part of it to decompose to the atomic form to produce activation, then for copper, whose amount is from 4 to 6 orders lower than the amount of zinc sulfide, it is necessary, for activation to take place, that a considerable part of what was added undergo decomposition. The cited work of Riehl [2,7], which asserts that activation with copper takes place as low as 400°, makes it clear that only a very energetic process of decomposition

can result in activation.

In the work of Strange [9] it is shown that when zinc sulfide is roasted in the absence of oxygen and "flux", and activated with a small amount of copper sulfide, the luminescent condition is not attained. Upon adding even a small amount of ammonium chloride (or other flux) the luminescent condition is obtained. We verified this work, and confirmed the fact that in the complete absence of a flux it is actually impossible to obtain the luminescent condition even in the presence of such a powerful activator as copper. It is understood that during the verification of this statement the copper was added in the form of the sulfide, obtained in an alkaline sulfide medium and well washed, as even very small amounts of chlorides result in the production of the luminescent preparations.

This fact, as well as the fact that the dissociation pressure of copper chloride, even at 450°, amounts to 25 mm, and at 520° to 650 mm, indicates that the activation by copper takes place in accord with reaction (6).

S U M M A R Y

On the basis of experimental work, an explanation is given for the fact that the production of luminescent zinc sulfide in the absence of an activator depends on the method of precipitating the sulfide. A method for the preparation of zinc sulfide and zinc-cadmium sulfide luminophores is described, with the illumination corresponding to only a single activator at its different concentrations. A review of the experimental results leads to the conclusion that the chemical mechanism for the activation of zinc sulfide by atomic zinc is similar to the chemical mechanism of its blackening under the action of light. Considerations are presented on the chemical mechanism of the activation of zinc sulfide by copper, and on the role of the flux in this process.

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THE REDUCTION OF SILICOTUNGSTATES WITH HYDROGEN

I. POTASSIUM TUNGSTEN BRONZE

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1. Tungsten bronze was obtained more than a hundred years ago, but despite the considerable interval that has elapsed since its discovery, it still has not been sufficiently investigated. The insolubility of tungsten bronze in the usual solvents, its decomposition upon heating, and its other properties make its investigation a complicated task. The purpose of our first communication is the study of the potassium bronze. This bronze was obtained by Laurent [1] by the reduction of potassium acid tungstate with hydrogen.

The author showed that the compound obtained had the form of splendidly formed shining prismatic crystals with a blue-violet color; Laurent did not carry out an analysis of the bronze obtained. Later, Zettnov [2], by electrolyzing potassium polytungstate, obtained blue-violet crystals in the form of prisms with a square cross section, with a characteristic coppery luster. Zettnov assigned to the potassium bronze crystals the composition $K_2O \cdot 4WO_3$; later on, Zettnov's formula was not confirmed by Knorre [3]. The latter author subjected the potassium bronze to an entire series of investigations. He studied the reducing action of hydrogen and illuminating gas on different potassium tungstates. According to Knorre, the best results in obtaining a yield of pure potassium bronze were found when he reduced potassium tetratungstate. This gave him metallic tungsten along with the bronze.

Knorre also found that on reducing the polytungstates with tin the purest bronze was obtained from potassium ditungstate. However, it is necessary to point out that in the reduction of the polytungstate with tin, the yield of bronze is considerably lower than in the reduction with hydrogen. Well crystallized bronzes were obtained by Knorre by means of the electrolysis of molten potassium ditungstate. In this process, the bronze separated at the cathode. Knorre determined the specific gravity of the bronzes obtained by electrolysis and by reduction with hydrogen. The specific gravity of the bronzes obtained by electrolysis (average of 3 determinations) was 7.135; that of the bronzes obtained by reduction (result of 2 determinations) was 7.095 and 7.085.

Independently of the nature of the reducing agent and of the original raw material that Knorre used, he always obtained only one potassium bronze, with the composition $K_2W_4O_{12}$. The results of the analysis of different preparations of Knorre are compared with those calculated from the formula, and are listed in Table 1.

TABLE 1

Calculated from the formula (%)	Found (%)	
WO_3 92.25,	92.72-92.00,	92.79-92.23.
K_2O 9.34	9.00-9.46,	9.03-8.91.

Later, Hallopeau [4] studied the reduction of potassium paratungstate with hydrogen and obtained a bronze with the composition $K_2W_3O_9$.

Analysis of the bronze gave K_2O contents of 12.37 and 11.51%. W, 71.36 and 71.95%. Upon reducing potassium paratungstate with tin, Hallopeau obtained a dark blue bronze with the composition $K_2W_5O_{14}$. Analysis for K_2O gave 7.33%, with a content of 75% W.

Inasmuch as the results of Hallopeau did not agree with the observations of Knorre, the latter suggested that Schaefer [5] once more verify the reaction for obtaining potassium bronze by the action of different reducing agents, and at the same time shed some light on the contradiction that had arisen.

Schaefer reduced potassium tetratungstate with hydrogen and illuminating gas; in both cases he obtained the ordinary potassium bronze $K_2W_4O_{12}$. Analysis showed that this had a content of W 73.18, 73.57, and 73.41%, and of K_2O 9.13, and 9.34%. Upon reducing potassium paratungstate with hydrogen, Schaefer obtained a bronze of the same composition, i.e., $K_2W_4O_{12}$. In the sample he obtained, he found W 73.29% and K_2O 8.91%. Reduction of the polytungstates with tin also gave him ordinary potassium bronze, in which Schaefer found W 72.60 and 73.93%. The content of K_2O was 9.89 and 8.54%. Calculations according to the formula used by Schaefer give W 73.15% and K_2O 9.34%.

Analysis of the data in the literature led us to the conclusion that in reality there was a single potassium bronze with the composition $K_2W_4O_{12}$. Despite the tremendous difficulties of analysis, the experiments of Knorre and Schaefer gave completely satisfactory agreement between the found and the calculated contents of the various components in the bronze. The data of Hallopeau on the existence of a blue potassium bronze were dubious. It seemed most probable that there was a single potassium bronze with the composition $K_2W_4O_{12}$, which might be considered an individual chemical compound.

2. We obtained potassium tungsten bronze by reducing potassium paratungstate with dry electrolytic hydrogen. As starting material, we used potassium paratungstate with the following composition: WO_3 80.8%, K_2O 13.51%, H_2O 4.6%, Cl 1.09%.

The reduction was carried out in electric ovens in molybdenum boats at a temperature of 620° , the substance being kept at this temperature for 1 hour.

Reduction gave fine violet crystals with a metallic luster, to the amount of 600 g. This was then treated with hot distilled water until all the chloride ion was removed.

After drying at 200° , grinding, and sifting through a 200 mesh sieve, the crystals were subjected to analysis, whose results are shown in Table 2.

It is clear from Table 2 that we obtained an individual preparation of the potassium bronze, corresponding accurately to the composition $K_2W_4O_{12}$.

The bronze obtained was subjected at the same time to X-ray analysis.

The X-ray analysis was kindly carried out by M.A. Vladimirova, who had previously shown that the potassium bronze had a tetragonal lattice with parameters $a = 4.67$ A, $c = 6.81$ A; $c/a = 1.46$.

The investigation was carried out in a Debye chamber with diameter 57.6 mm;

TABLE 2

Chemical analysis of potassium bronze

	K_2O , %	W, %
Found	9.53	73.06
$K_2W_4O_{12}$. Computed	9.34	73.16

the anticathode was of copper, the voltage was 30 kv, the current strength 8 ma, and the duration of exposure 6 hours.

Calculations of the roentgenogram of the violet potassium bronze we had obtained showed that it could also be referred to a tetragonal lattice with the parameters indicated (see calculations in Table 4).

The roentgenogram was also a standard for characterizing the products obtained by the reduction of different potassium silicotungstates with hydrogen.

The bronze was subjected to further reduction with hydrogen at a higher temperature, in this way we attempted to trace the possible decomposition of the bronze during reduction.

We controlled the process of decomposition of the bronze by chemical analysis of the reduced sample, using washing with alkali. The reduction proceeded according to the equation:



The reduction was carried out under the same conditions as the preparation of the bronze. Only the temperature was changed. The results of reduction are shown in Table 3.

TABLE 3

The reduction of potassium bronze with the composition $\text{K}_2\text{W}_4\text{O}_{12}$ by hydrogen

No. of expt.	Temperature of reduction (°C)	Time in oven (hours)	Chemical analysis	
			Total K_2O (%)	K_2O washed out (%)
1	Original bronze	—	9.54	0.32
2	700	1	9.54	4.39
3	750	1	9.54	8.35
4	800	1	9.54	8.86

TABLE 4

Calculation of roentgenogram of potassium bronze

No. of line	Intensity	Observed $\sin^2 \theta$	hkl	$\sin^2 \theta$ calculated for tetragonal lattice with parameters $a = 4.67$, $c = 6.81$
1	Strong	0.061	011	0.063
2	Strong	0.081	110	0.085
3	Average	0.103	111	0.105
4	Strong	0.123	102	0.123
5	Average-weak	0.163	003	0.162
6	Average	0.180	200	0.177
7	Strong	0.247	202	0.250
8	Average-strong	0.270	113	0.267
9	Very strong	0.295	212	0.294
10	Very strong	0.363	221	0.362
11	Strong	0.443	131	0.447
12	Weak	0.494	204	0.495
13	Average	0.505	312	0.508
14	Very strong	0.553	320	0.556
15	Strong	0.670	224	0.667
16	Strong	0.704	402	0.704
17	Strong	0.708	304	0.708

Analysis of the wash alkali showed that at a temperature of 700° there was definite decomposition, which was almost complete at a temperature of 800°.

SUMMARY

1. Reduction of potassium paratungstate with hydrogen gave a potassium bronze with the composition $K_2W_4O_{12}$.
2. It was found that upon reduction with hydrogen in the temperature interval from 700 to 800°, the potassium bronze decomposed to give soluble potassium tungstate and metallic tungsten.
3. An X-ray investigation of the potassium bronze has been carried out; it has been found that it has a tetragonal lattice with parameters: $a = 4.67$ and $c = 6.81$ Å.
4. Analysis of the data in the literature, and the results of our own experiments lead us to believe that there is a single potassium bronze, which may be regarded as an individual chemical compound.

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1. THE MECHANISM OF OXIDATION OF NITRIC OXIDE IN DIFFERENT DISCHARGES

T. V Zabolotsky*

The oxidation of nitrogen in a discharge has been studied by N.Kobozev, M. Temkin, and S. Fraiberg [1]. However, in view of the great interest in accelerating this reaction and in studying its mechanism, we undertook an investigation under various conditions of discharge. With this purpose we used induction, low-frequency, and high-frequency fields, as well as the corona discharge, which took place at atmospheric pressure.

The temperature of the gas in the reaction space was measured with a toluene thermometer, and the duration of the reaction, as usual, was determined by the graduations of the reaction volume according to the velocity of the gas per second. The differential determination of the oxides of nitrogen was carried out by an oxygen method, in which the degree of oxidation was calculated from the kinetic reaction equation: $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$. The influence of the discharge upon the velocity of oxidation of the oxide was determined by comparing the results obtained for oxidation ($\alpha_{\text{expt.}}$) in the electric field and outside it. The initial composition of the gases used varied considerably.

Below are listed, briefly, the results of the experiments.

A comparison of the degree of oxidation ($\alpha_{\text{expt.}}$), as can be seen from the following data, shows that the induction field has no accelerating action on the oxidation of nitric oxide:

Composition of nitrogen oxides (in %)		
	Outside field	In induction field
NO_2	0.38	0.36
NO	1.02	1.22
$\text{NO}_2 + \text{NO}$	1.35	1.58
$\alpha_{\text{expt.}}$	24.0	22.8

The oxidation of nitric oxide in a high-frequency field was studied both in illuminated and unilluminated fields; we considered the case one of unilluminated high-frequency discharge when the voltage corresponded to the threshold for ignition, but no illumination was produced between the electrodes.

It was shown that in both cases, there was no acceleration of the oxidation of nitric oxide, as follows from the following data:

* Z. V. Morozova took part in the experimental work.

Unilluminated		High-frequency field		Illuminated	
Composition of nitrogen oxides, %					
Outside field		In field	Outside field		In field
NO ₂	0.39	0.35	0.37		0.26
NO	1.12	0.98	1.10		0.84
NO ₂ + NO ..	1.51	1.33	1.47		1.10
$\alpha_{\text{expt.}}$	25.8	26.3	25.0		23.6

In the corona discharge of the low-frequency field, the experiments were carried out by the same method as used for the high-frequency field.

The experimental data listed below show the same results:

Composition of nitrogen oxides, %			
Outside field		In corona field	
NO ₂	0.27	0.32	
NO	0.50	0.69	
NO ₂ + NO	0.77	1.01	
$\alpha_{\text{expt.}}$	35.0	31.6	

Like the high-frequency field, the low-frequency corona field showed no influence in accelerating the oxidation of NO. In order to obtain a more complete understanding of the action of an electric field on the oxidation, experiments were carried out using mixtures of nitrogen oxides with previously ozonized oxygen-containing gases.

We used the same apparatus for this purpose, carrying out the ozonization of the oxygen-containing gases in the reaction tube. The nitric oxide was mixed with these gases in the reaction tube behind the discharge tube. Here we list the results of the experiments.

Composition of nitrogen oxides after reaction					
Mixed with unozonized air			Mixed with ozonized air		
NO ₂	1.08	11.50	1.10		13.70
NO	0.32	2.80	0.00		0.30
NO ₂ + NO	1.40	14.30	1.10		14.00
$\alpha_{\text{expt.}}$	77.3	80.4	100.0		98.0

As can be seen from this table, when the nitric oxide is mixed with ozonized air, a considerable acceleration of the reaction is observed, so that 100% oxidation is attained.

In this process, the rapid conclusion of the reaction takes place even when the nitric oxide reaches a high concentration, up to 14%, that is, when the ratio of the ozonized oxygen of the air to nitric oxide equals:

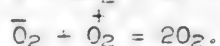
$$\frac{\text{O}_2 \text{ ozonized}}{\text{NO}} = 1.4.$$

In our experiments using this method with the corona discharge, the ozone content in the air amounted to an average of 1.0%.

As can be seen from these data, the different forms of discharge and induction fields do not result in any acceleration of the oxidation of nitric oxide. This is confirmed by a comparison of the degree of oxidation of nitric oxide in experiments carried out in the discharge with experiments carried out outside the discharge.

However, acceleration does take place if the oxidation of the nitric oxide is first carried out with ozonized oxygen or oxygen-containing gases. This agrees with the results obtained by N. Kobozev, M. Temkin, and S. Fraiberg.

The absence of acceleration under the direct action of the discharge, and its presence during the subsequent oxidation with ozonized oxygen, are of great interest. Here we may consider only a single hypothesis: the acceleration of the oxidation takes place because of the ozone, which is not formed in the discharge of the gas mixture in the presence of nitrogen oxides. The well known facts of the decomposition of ozone by chlorine, bromine, and hydrogen bromide were explained by N. Semenov [2] as due to the catalytic properties of these substances. As for the influence of nitrogen oxides on the ozone under the conditions of the discharge, this is to be referred, apparently, to an action similar to that which takes place during the oxidation of hydrogen and carbon monoxide, as A. Kovalsky, A. Zagulin, and N. Semenov [3] have shown. Under these conditions, nitrogen dioxide in high concentrations may be regarded as a negative homogeneous catalyst, which does not break down the ozone (formed in the discharge across the ions of oxygen) but hinders its formation approximately according to this mechanism:



Thus, there takes place a rupture of the chain which leads to the formation of ozone, and therefore the acceleration of the oxidation is also absent. As for the subsequent oxidation of nitric oxide by ozone in a homogeneous medium, here, in considering the mechanism, we differ from the conclusions of N. Kobozev, M. Temkin, and S. Fraiberg, who suggested one of the most complicated reactions:



which takes place in the steps:



The lack of correspondence between the rapid course of the reaction (according to the observation of these authors) and the complicated and polymolecular nature of these equations makes this impossible.

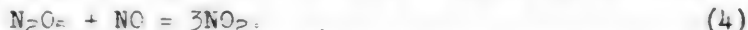
It is most probable that simpler reactions for the oxidation of nitric oxide take place:



or



as in this latter case the pentoxide reacts rapidly to give the dioxide:



The obvious nature of this hypothesis is very well indicated by the decomposition of ozone. According to our results, as has been shown above, the decomposition of ozone is much less than is required by the reaction (1) ($O_3/NO = 1.5$), and amounts in all to only O_3 ozone.

1. The direct passage of a spark across various electrical and induction

fields does not result in the acceleration of the oxidation of nitric oxide.

2. The acceleration of the oxidation of nitric oxide takes place only during its subsequent mixture with ozone or ozonized oxygen-containing gases.

3. A hypothesis has been suggested to explain why the velocity of oxidation of the nitric oxide is not increased in the discharge. This includes the breakdown by nitrogen dioxide of the chains needed for the formation of ozone.

4. A hypothesis has been suggested for the mechanism of oxidation of nitric oxide by ozone in a homogeneous system.

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II. THE MECHANISM OF OXIDATION OF MICROCONCENTRATIONS OF NITRIC OXIDE IN THE CORONA DISCHARGE*

T. V. Zabolotsky and S. N. Solnishkova

The oxidation of micro concentrations of nitric oxide present in various gas mixtures is of considerable practical significance.

As is known, the velocity of oxidation of such amounts of nitric oxide at low concentrations of oxygen in gas mixtures is practically zero. The purpose of this paper was to study the mechanism of oxidation of nitric oxide at micro concentrations in the corona discharge.

The reaction took place in a discharge tube of an ozonator type, to which an alternating current of technical frequency was applied. Through the ozonator there were passed various gas mixtures (H_2 , N_2 , O_2) previously found to contain nitric oxide in micro amounts. These were obtained by numerous "dilutions" of nitric oxide with the gas mixture.

The velocity of the gas current was regulated with a graduated rheometer. The gas mixture that had gone through the discharge tube was analyzed first for its content of micro amounts of nitric oxide, according to the colorimetric method of Gurevich [1], which we used under dynamic conditions, then for its ozone content with iodine, and finally for its O_2 and H_2 contents.

Below are listed the results of several experiments.

TABLE 1

Expt No.	Composition of gas mixtures after reaction							Degree of oxidation α
	O_2	H_2	N_2	O_2	NO	NO ₂	N ₂ O ₅	
	%	%	%	%	pM	pM	pM	
1	1.6	93.5	5.2	0.000	1.76	1.44	0.00	45.0
2	1.7	91.5	6.8	0.000	2.15	2.15	0.00	50.0
3	2.5	87.5	10.0	0.000	2.30	2.30	0.00	50.0
4	4.0	80.0	16.0	0.002	0.52	0.52	0.00	50.0
5	5.0	75.0	20.0	0.006	0.45	1.05	0.00	70.0
6	7.0	65.0	28.0	0.007	0.00	1.89	1.23	100.0
7	8.0	60.0	32.0	0.015	0.00	1.49	1.27	100.0
8	11.0	45.0	44.0	0.040	0.00	1.20	0.65	100.0
9	11.0	85.0	4.0	0.005	0.45	1.21	0.00	80.0

As can be seen from the results listed, the degree of oxidation of the micro quantities of nitric oxide in the corona discharge depends on the composition of the gas, and fluctuates from 50.0 to 100.0%.

*At microconcentrations we used parts per million (pM) of nitric oxide in the gas mixture.

As has been shown in one of our articles [2], the acceleration of the process of oxidation of macro concentrations of nitric oxide takes place only because of ozone. The same thing holds in this case as well, with this difference, however, that oxidation takes place directly in the ozonator, as the negligible concentrations of nitrogen dioxide apparently have no negative action on the formation of ozone in the discharge, as was the case at macro concentrations of NO_2 in the investigation cited above.

The dependence of the degree of oxidation of micro concentrations of nitric oxide on the composition of the gas in the corona discharge, with a constant current, temperature of 24° in the reaction space, and velocity of gas passage of 200 cc per minutes, is shown in Table 1.

Thus, in the discharge, the complete oxidation of micro amounts of nitric oxide is possible. It is the result of the presence of ozone, and takes place, in accordance with our hypothesis, according to the equations:



The oxidation of nitric oxide takes place according to reaction (1); when there is incomplete oxidation of the nitric oxide ($\alpha = 50$ to 70%) the free NO reacts with N_2O_5 according to equation (2).

This is evident from Table 1, where the concentration of ozone is given in column 5. In the first three experiments, no nitrogen pentoxide or ozone were observed. Even with a slight excess of ozone - 0.002 to 0.006% (Experiments 4 and 5)) there was still no N_2O_5 observed. This began to appear only at an ozone concentration of 0.007%, at which 100% oxidation took place. The decrease in the amount of O_3 in the final gas to below 0.006% led to a drop in the degree of oxidation and to the using up of the N_2O_5 (Experiment 9). The completeness and the velocity of oxidation of the nitric oxide depended, thus, on the velocity of formation of ozone, and the latter in its turn depended on the concentration of oxygen and hydrogen in the gas mixtures.

With an increase in the content of oxygen in the gas mixture, the concentration of ozone formed increased. In order to complete the oxidation of micro amounts of nitric oxide, the oxygen content had to be about 7.0% when there was 65.0% of hydrogen.

If there is a greater amount of hydrogen in the gas mixture (from 65.0 to 95.0%) much more oxidation of it by ozone takes place. This must be kept in mind in determining the amount of ozone needed to oxidize the NO. This is clear from Experiment 9, where the increase of oxygen even up to 11.0%, at high concentrations of hydrogen (85.0%) does not lead to the complete oxidation of nitric oxide ($\alpha = 80\%$).

From all this it is clear that for complete oxidation of micro concentrations of nitric oxide in gases that contain hydrogen, the amount of ozone formed in the discharge must be greater than that stoichiometrically needed for reaction (1), where $\text{O}_3/\text{NO} = 0.5$, as a result of its decomposition in the oxidation of the hydrogen.

The accelerating action of the electrical discharge on the oxidation of micro quantities of nitric oxide is clear from the data for the comparative oxidation (other conditions being the same) outside the electrical field and in the electrical field (Table 2). In this case, we took nitrogen as our original gas, with a content of 1.5% oxygen and the NO in parts per million.

Where in the absence of an electrical discharge the degree of oxidation, α , is only 8.0 to 10.0%, in the discharge it reaches 100%.

In the absence of hydrogen in the original mixture the concentration of oxygen needed to oxidize the NO decreases. Thus, instead of 5.0% in the gas mixture containing 65.0% H₂ (Experiment 6), the same oxidative effect was reached in the mixture without hydrogen with 1.5% O₂. In the final gas thus obtained, there was the same amount of ozone (0.007%).

The increase in the total of nitrogen oxides in the gas mixture used in the experiments (Table 2) carried out in the electrical discharge (10.83 to 11.50 pM instead of 2.67 to 2.80 pM) is to be explained by their formation in the electrical field.

TABLE 2

Content of nitrogen oxides after reaction (in pM)									Ozone content
In absence of electrical field				In electrical field					
NO	NO ₂	NO + NO ₂	α %	NO	NO ₂	N ₂ O ₅	total oxides	α %	O ₃ %
2.40	0.27	2.67	10.0	0.00	8.00	2.83	10.83	100.0	0.007
2.57	0.23	2.80	8.2	0.00	11.50	11.50	11.50	100.0	0.007

The correctness of the mechanism suggested for the oxidation of micro concentrations of nitric oxide is also confirmed by experiments carried out with a gas mixture (containing micro concentrations of nitric oxide) mixed with both previously ozonized and unozonized air. This can be seen from the following data (Table 3).

TABLE 3

Gas composition: 56% O₂, 60-65% H₂ and 30-35% N₂

Content of nitrogen oxides after reaction (in pM)							
Mixed with unozonized air				Mixed with ozonized air			
NO	NO ₂	NO + NO ₂	α %	NO	NO ₂	NO + NO ₂	α %
6.40	2.60	9.00	29.00	2.16	14.90	17.00	87.5
4.50	1.55	6.05	25.5	7.50	21.00	28.50	73.5

These data show that although mixing with a previously ozonized gas accelerates oxidation, it has no advantage over the method of direct oxidation in the discharge.

In the latter case, the oxides of nitrogen formed during the ozonization of the air are increased in initial concentration.

SUMMARY

1. The conditions for the oxidation of micro concentrations of nitric oxide in the corona discharge have been studied.
2. Acceleration of the oxidation of micro concentrations of nitric oxide in the corona discharge takes place because of the ozone, and is determined by the velocity of formation of the latter under these conditions.
3. Micro concentrations of nitrogen dioxide in the gas mixture do not act as a negative catalyst with regard to ozone, in the way they act at macro concentrations.
4. The completeness of oxidation of micro concentrations of nitric oxide is determined by the concentration of ozone, whose ratio to the nitric oxide should be not less than O₃/NO = 0.5.

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III THE CATALYTIC ROLE OF OZONE IN THE OXIDATION OF NITRIC OXIDE

T. V. Zabolotsky

In an investigation of the oxidation of nitric oxide in the electrical discharge [1] we suggested a hypothesis concerning the mechanism of oxidation of nitric oxide by ozone in a homogeneous medium. However, further investigation of this reaction led to new ideas.

In reality, the mechanism of oxidation of nitric oxide by ozone is much more complicated than has been accepted in picturing different reactions, and does not correspond quantitatively to them.

Thus, according to the proposed reaction of N. Kobozev, M. Temkin, and S. Fraiberg [2], in the oxidation of nitric oxide:



the ratio of O_3/NO amounts to 1.5, while in the reaction suggested by us [1]



this ratio equals unity.

In actuality, the amount of ozone expended in oxidizing the nitric oxide is considerably less.

We shall give one of our experiments on the oxidation of nitric oxide with ozone.

In the oxidation of an air-nitric oxide mixture containing 14.0% of NO, the degree of oxidation reached 80.0%, while under the same conditions the oxidation of NO with air which had undergone preliminary ozonization (i.e., the NO was mixed with ozonized air) at the same concentration amounted to 100.0%.

The initial composition of the air-nitric oxide mixture in these experiments was as follows: NO 13.2%, O_2 18.3%, N_2 68.5%.

Under the conditions of our experiments, ozonization produced about 1.0% of ozone. In this case the ratio of ozonized oxygen to NO (not of ozone), was

$$\frac{\text{O}_2 \text{ ozonized}}{\text{NO}} = \frac{18.3}{13.2} \cdot \frac{0.01}{1} = 0.014.$$

This indicates, in the first place, that the reaction takes place fundamentally because of the oxygen, with the ozone accelerating it, and in the second place, that the overall reaction takes place to give nitrogen dioxide.



or



We must here point out that in the experiments of N. Kobozev, M. Temkin, and S. Fraiberg [2] also, as well as in those of other investigators who used oxygen or air which contains ozone will be called ozonized.

ozonized gases (oxygen or air) the ozone content was also low, and fluctuated from 1.0 to 2.0%.

In the work we have cited [1] the improbability of reaction (1) was shown. To this we must add that it is impossible to have a rapid reaction merely because of the ozone, which amounts in all to a hundredth part of the oxygen, and to almost the same fraction of the amount stoichiometrically necessary.

Consequently, oxygen has a dominating role in the oxidation of nitric oxide with ozonized gases, and not a secondary one, as is postulated in mechanisms (1) and (2). We are forced to the conclusion that it is very probable that the influence of the ozone is a catalytic one, hastening the process of oxidation by means of the formation of intermediate products, which have been found by Sprenger [3], using a spectroscopic method, to be produced in the form of NO_3 .

It is possible to have a mechanism for the catalytic reaction such as:



where the ozone is formed again and begins a new chain.

SUMMARY

1. An analysis has been given of the mechanism of oxidation of nitric oxide with ozone.

2. A hypothesis has been suggested concerning the catalytic oxidation of nitric oxide by ozone, and a mechanism of oxidation has been given.

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THE INAPPLICABILITY OF BODENSTEIN'S KINETIC EQUATION TO THE OXIDATION OF NITRIC OXIDE UNDER DYNAMIC CONDITIONS

T. V. Zabolotsky*

It is known that the oxidation of nitric oxide to give the dioxide is described by a reaction of the third order:

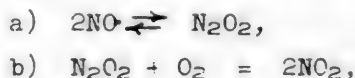


In this oxidation, a straight-forward reaction prevails up to 200-250°. This is proportional to the product of the square of the concentration of nitric oxide by the concentration of oxygen:

$$\frac{dC_{\text{NO}_2}}{dt} = K_1 C_{\text{NO}}^2 C_{\text{O}_2}. \quad (1)$$

The velocity constants studied by Bodenstein [1,2,3] in accordance with this equation are ordinarily used both for research and in industrial practice, and they sometimes serve as characteristics for comparing the catalytic oxidations of nitric oxide. However, the conditions under which Bodenstein studied the velocity of oxidation of nitric oxide give no grounds to consider that the results he obtained are universally valid. He used gas mixtures (NO and O₂) in great volume, using a glass stirrer and pressures below the atmospheric. This cannot be compared with the dynamic current method widely used in research. The results obtained in these experiments cannot be compared with the results obtained under dynamic conditions, especially at great velocities of passage of the gas, and at atmospheric pressure.

It is also possible to assume that the mechanism of oxidation of nitric oxide proposed by Bodenstein [3] for homogeneous conditions, by means of the dimer:



does not take place under dynamic conditions.

Numerous experiments carried out by us for the purpose of testing the applicability of an equation of the third order to the oxidation of nitric oxide and of Bodenstein's velocity constants under dynamic conditions confirmed our assumptions. The velocity of oxidation of nitric oxide by the dynamic method was measured by passing the gas mixture through open glass tubes (as well as through tubes filled with activated carbon) with a definite diameter and volume. The mixing of the reacting gases was also carried out in these. The time of reaction was determined, as usual, per unit of reaction volume by the volume of gas passed per second through the tube, the volume of the tubes leading the gas away for analysis also being taken into account. The nitric oxide was obtained by the decomposition of sodium nitrate with sulfuric acid. The oxygen was taken from a

* A. V. Zaltshtein and Z. V. Morozova took part in the work.

tank. The velocity of the gases, and their ratios, were determined by a rheometer after they had first been dried with concentrated sulfuric acid (sp. gr. 1.84) and phosphorus pentoxide. The temperature of the reaction volume was kept constant by means of a thermostat. The analysis of the separate determinations of nitrogen oxides was carried out by an acid method. To calculate the extent of oxidation (α_{theor}), we used equation (1), expressed in the well-known integral form. The results of the experiments are given in the tables below and in the graphs.

TABLE 1

The oxidation of nitric oxide with an initial gas composition of: N_2 97.0%, NO 0.3-1.0%, O_2 1.3%; constant time of reaction, and a temperature of 20°.

Composition of nitrogen oxides after reaction			$\alpha_{\text{expt.}}$	$\frac{\alpha_{\text{expt.}}}{\alpha_{\text{theor.}}}$
NO	NO_2	NO + NO_2		
0.20	0.17	0.37	46.0	25.0
0.19	0.15	0.34	44.0	25.0
0.25	0.23	0.48	48.0	24.0
0.30	0.30	0.60	50.0	20.0
0.41	0.39	0.80	48.7	16.0
0.45	0.55	1.00	55.0	14.0

TABLE 2

The oxidation of nitric oxide with an initial gas composition of: N_2 78.8%, NO 2.0%, O_2 19.2%; constant time of reaction, and a temperature of 20°.

Composition of nitrogen oxides after reaction			$\alpha_{\text{expt.}}$	$\frac{\alpha_{\text{expt.}}}{\alpha_{\text{theor.}}}$
NO	NO_2	NO + NO_2		
0.61	1.44	2.05	70.2	1.4
0.60	1.38	1.98	69.2	1.4
0.64	1.36	2.00	68.0	1.4
0.61	1.43	2.04	70.0	1.4
0.60	1.40	2.00	70.0	1.4

In the table are given the results obtained in the differential determination of nitric oxide after the reaction; on the basis of these data, the Bodenstein constants for the degree of oxidation, $\alpha_{\text{expt.}}$, have been calculated. In the last column of the table are listed the ratios of the experimental degrees of oxidation to the theoretical, calculated for the conditions of the experiment by an equation of the third order and the Bodenstein constants $\alpha_{\text{expt.}}/\alpha_{\text{theor.}}$. As can be seen from this column, $\alpha_{\text{expt.}}$ is much greater than $\alpha_{\text{theor.}}$, approximately 12 to 25 times as great. In order to make clear the influence of the concentration of the initial gas on the velocity of oxidation of nitric oxide, we carried out experiments whose results are shown in Table 2.

As can be seen from Tables 1 and 2, as the concentration of oxygen in the gas mixture increases, the experimentally found degree of oxidation approaches the theoretical value.

The dependence of the ratio $\alpha_{\text{expt.}}/\alpha_{\text{theor.}}$ on the duration of reaction and on the initial composition of the gas is shown in Table 3.

The same dependence is shown in Figs. 1 and 2.

On the basis of the results given for the oxidation of nitrogen oxides, we may draw the conclusion that deviations of Bodenstein's results from the results obtained in dynamic experiments is greater the greater the velocity of the gas stream, (lower reaction

TABLE 3

Duration of reaction, seconds	Initial composition of gases	
	N_2 97.0% O_2 1.5% NO 0.15%	N_2 79.5% O_2 19.0% NO 1.5%
τ	$\frac{\alpha_{\text{expt.}}}{\alpha_{\text{theor.}}}$	$\frac{\alpha_{\text{expt.}}}{\alpha_{\text{theor.}}}$
1.0	20.0	2.0
3.5	10.0	1.8
1.5	8.0	1.5
8.0	7.0	1.4
13.0	5.0	1.3
21.0	3.0	1.2
35.0	2.0	1.1

time) and the lower the concentration of oxygen.

As the results of the catalytic oxidation of nitric oxide are usually compared with the theoretical values obtained by calculation according to the data of Bodenstein, it appeared not without interest to carry out this comparison experimentally. With this purpose, we carried out several series of experiments whose results are listed below.

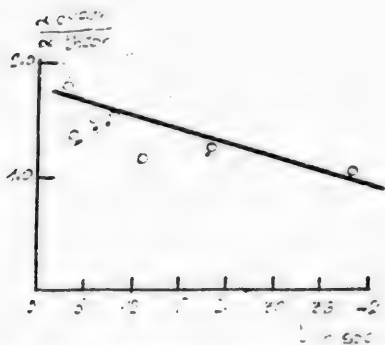


Fig. 1. Relationship of $\frac{\alpha_{\text{exper.}}}{\alpha_{\text{theor.}}}$ to time of reaction for air-gas mixtures containing 1.0 to 1.5% NO.

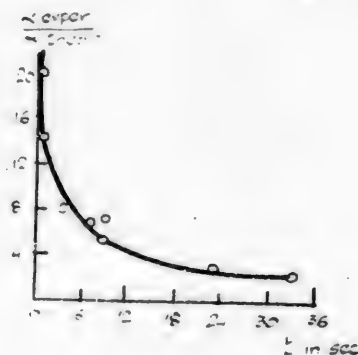


Fig. 2. Relationship of $\frac{\alpha_{\text{expt.}}}{\alpha_{\text{theor.}}}$ to time of reaction for gas mixtures containing 1.5% O_2 , 97.0% N_2 , and 1.0-1.5% NO.

TABLE 4

The comparative oxidation of nitric oxide with an initial composition of N_2 97.5%, O_2 1.5%, and NO 1.0%, constant time of reaction, and a temperature of 20°

Without catalyst		Over catalyst		
$\alpha_{\text{exper.}}$	$\alpha_{\text{exper.}}/\alpha_{\text{theor.}}$	$\alpha_{\text{catal.}}$	$\alpha_{\text{catal.}}/\alpha_{\text{theor.}}$	$\alpha_{\text{catal.}}/\alpha_{\text{exper.}}$
44.0	22.0	90.0	45.0	2.0
46.0	23.0	96.0	47.0	2.1
49.0	20.0	98.0	48.5	2.0
50.0	14.0	99.0	49.0	2.0
The same for gas composition N_2 78.8%, O_2 19.2%, NO 2%.				
70.2	1.4	91.5	1.8	1.30
69.5	1.4	93.5	1.8	1.34
68.0	1.4	94.5	1.8	1.38
70.0	1.4	97.0	1.9	1.38

In this case the method of investigation remained the same as in the preceding experiments, with the sole difference that the gas mixture was passed into two reaction tubes placed in parallel, one of them being filled with activated carbon. All the conditions, including reaction time, were kept the same in both tubes. The comparison, as in the preceding cases, was carried out with the $\alpha_{\text{theor.}}$ calculated according to the data of Bodenstein (Table 4).

The last column of Table 4, $\alpha_{\text{catal.}}/\alpha_{\text{exper.}}$, determined the actual catalytic activity of the activated carbon, which corresponded to 1.3 to 2.0 A

comparison of the catalytic activity of the activated carbon by means of the ratio $\alpha_{\text{catal}}/\alpha_{\text{theor.}}$ was absolutely incorrect (according to our data, $\alpha_{\text{catal}}/\alpha_{\text{theor.}}$ varied from 1.8 to 50.0). The latter fact also permitted us to explain the great activity of the activated carbon obtained by Burdick [4] (1000-fold acceleration), Chego and Guassi [5] (20-fold acceleration), N.P.Kurin and I.O.Blokh [6] (from 5 to 6-fold), and the apparently correct determination of G.K.Boreskov and S.M. Shogam [7], according to whose data the acceleration was only 2 or 3 fold.

An analysis of our results with regard to the velocity of oxidation of nitric oxide under dynamic conditions leads to the following conclusions:

1. The mechanism of this reaction under dynamic conditions is different from that under homogeneous conditions, for which Bodenstein's velocity constants were obtained.

2. The equation for a reaction of the third order is applicable under limited conditions, when there is a slow gas current and the gas mixture contains a great amount of oxygen.

3. As the velocity of the gas current increases, the streaming of the gas begins to play a role which strongly favors an increase in the number of molecular collisions between the molecules themselves and with the walls of the reaction tubes.

4. This last fact is of great significance. It brings the mechanism of this process close to the catalytic mechanism, and suggests a homogeneous-heterogeneous mechanism.

5. A comparison of the velocity of catalytic oxidation of nitric oxide with the velocity in the absence of a catalyst under dynamic conditions gives the actual activity of the catalyst, which for activated carbon amounts to from 1.3 to 2.0.

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THE COMPLEX OF UNIVALENT COPPER WITH THIOCYANATE

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It has been shown in the literature [1,2] that bivalent copper and alkali metal thiocyanate form a precipitate which is easily decomposed by water. The reaction gives the thiocyanate of univalent copper, which has a tendency to form complexes with an excess of thiocyanate.

In order to make a detailed investigation of this process and to determine the composition of the complex formed, we utilized a polarographic method of analysis. In addition, we considered it our task to determine the constants for the instability of the complex, and the approximate value of its heat of formation from the ions.

Technique of the Experiment

For the exposure of the polarogram we used a visual apparatus, fitted with a mirror galvanometer which had a current-sensitivity of 1.17 A/mm. Ordinarily we utilized 1/25th of the maximum sensitivity of the galvanometer.

The electrolytic vessel in which the solution to be analyzed was placed was supplied with a tube so that the solution could be blown through with a stream of hydrogen in order to remove the oxygen dissolved in it.

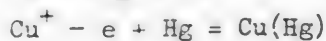
A saturated calomel half-element served as the anode. This was connected to the electrolyzer by means of siphons and a small beaker placed between them filled with a solution of potassium chloride. The potential of the saturated calomel half-element was arbitrarily taken as equal to zero. The electrolyzer, the intervening beakers, and the calomel half-element were placed in a liquid-filled thermostat, in which the temperature was maintained constant at $25 \pm 0.3^\circ$.

A mercury dropping electrode, constructed in the usual manner with a reservoir and a rubber stopper, had the characteristic $m^{2/3} \cdot t^{1/6} = 1.28 \text{ mg}^{2/3} \text{ sec}^{1/6}$.

In this work we used the usual analytical reagents.

EXPERIMENTAL

When the ions of bivalent copper are reduced on the mercury dropping electrode in the presence of potassium nitrate, used as an indifferent electrolyte, we can obtain a polarogram which consists of a single wave. This wave corresponds to the reduction of the hydrated ions of bivalent copper to the metal, which then forms a dilute amalgam. The half-wave potential in this case equals approximately -0.02 V with respect to the saturated calomel electrode. If to the solution of copper nitrate and potassium nitrate a solution of ammonium thiocyanate is added, then we can observe on the polarogram two waves, which in all probability correspond to the reactions.



with half-wave potentials of about -0.02 V and -0.4 V.

However, the total height of the wave is rather sharply decreased, and the formation of a white precipitate is observed. This precipitate is very well adsorbed on the surface of the mercury drops and makes the correct formation of the drops extremely difficult. It is very natural to assume that the decrease in the height of the copper wave is related to the decrease in the concentration of copper ions in the solution and to the formation of the precipitate from the latter. This picture is observed in those cases where the concentration of the ammonium or potassium thiocyanate does not exceed 0.3 to 0.5 N.

In the presence of more concentrated solutions which contain thiocyanate ions, the precipitate of copper thiocyanate, formed during the addition of the first portions of ammonium thiocyanate, is dissolved in the excess of precipitating agent, and the solution becomes transparent.

We investigated the reduction of the copper ions when these were used in a concentration of 0.33 mol./l, in the presence of ammonium thiocyanate whose concentration varied from 1 N to 6 N.

In order to suppress the maxima which had formed, we utilized a solution of agar-agar, whose addition, as was ascertained in a number of experiments, did not alter the potential of the copper wave.

In all cases, the polarogram showed a single wave, whose half-wave potential depended on the concentration of ammonium thiocyanate, and was displaced in the direction of more negative values when the content of thiocyanate ions in the solution whose polarogram was being taken was increased. The wave forms are shown in Fig. 1.

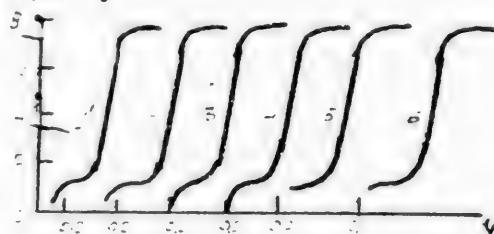


Fig. 1. Reduction wave of copper from solutions of ammonium thiocyanate at different concentrations.

1-concentration of ammonium thiocyanate 1N 2-2N
3-3N 4-4N. 5-5N. 6-6N.

We must observe that at a potential of the mercury drops of about -0.02 V, a diffusion current arises, whose value is proportional to the concentration of thiocyanate in the solution. It is easy to confirm the fact that this current is not related to the reduction of the copper ions, as it is maintained even in those cases where there is no copper in solution. Fig. 2 shows the diffusion waves: one of them (Curves 1 and 2) corresponds to the case where there were no copper ions in solution and the concentrations of ammonium thiocyanate equaled 1 N and 2 N, while the other (Curves 3 and 4) was taken after the addition of cuprous nitrate.

Table 1 gives the calculated values of the half-wave potential of copper at different concentrations of ammonium thiocyanate.

The influence of the temperature on the diffusion current and on the half-wave potential of copper was investigated for two solutions of ammonium thiocyanate, 1 N and 2 N. The results of the measurements are given in Table 2.

It can be seen from Table 2 that as the temperature rises, the diffusion

TABLE 1

The dependence of the copper half-wave potential on the concentration of ammonium thiocyanate

Concentration of ammonium thiocyanate (in g-equivs.)	$\pi_{1/2}$ (in volts)
1	-0.52
2	-0.59
3	-0.63
4	-0.67
5	-0.70
6	-0.72

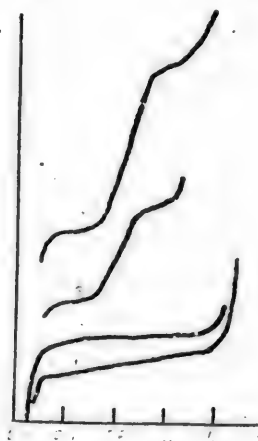


Fig. 2. Waves of univalent copper in the presence of ammonium thiocyanate and the ground waves. 1-ground in NH_4CNS 2-2N NH_4CNS 3 and 4-ground waves with different added amounts of univalent copper.

TABLE 2

The dependence of the diffusion current and the copper half-wave potential on the temperature. Concentration of copper 0.003 mol./liter

Temperature, °	$I_{\mu\text{A}}$	$\pi_{1/2}$ V
Concentration $\text{NH}_4\text{CNS} = 1 \text{ N.}$		
15	5.73	-0.52
25	7.02	-0.52
34	7.84	-0.52
42	8.66	-0.52
Concentration of $\text{NH}_4\text{CNS} = 2 \text{ N}$		
25	6.90	-0.59
33	8.31	-0.59
42	9.13	-0.59

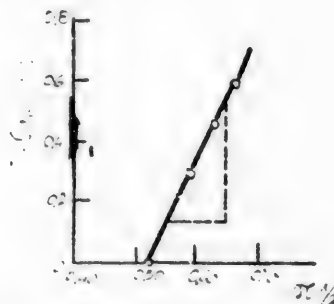


Fig. 3. The dependence of the half-wave potential of univalent copper on the logarithm of the concentration of ammonium thiocyanate.

current of the copper increases, while the half-wave potential remains unchanged.

Consideration of Results

When the bivalent copper ions react with the thiocyanate ions, the formation of the difficultly soluble compound of thiocyanate and bivalent copper takes place, with a velvety-black color. This compound is quickly decomposed by the action of water, and still more energetically in the presence of alkali metal thiocyanates or ammonium thiocyanate, with the separation of the thiocyanate of univalent copper, CuCNS , with a white color.

Cuprous thiocyanate, CuCNS , is practically insoluble in water, but dissolves in concentrated solutions of thiocyanates with the formation of a complex compound of the double salt type.

The addition of ammonium thiocyanate to a solution which contains the ions of bivalent copper leads to a decrease of their concentration in the solution and therefore to a diminution of the current. As in the presence of low concentrations of ammonium thiocyanate no complex is apparently formed, the diffusion current of copper does not increase.

The appearance of two waves on the polarization curve at low concentrations of ammonium thiocyanate is related to the simultaneous presence in the solution of bivalent copper ions which have not yet been precipitated, and univalent copper ions resulting from a certain solubility of the CuCNS . The origin of the first wave may also be related to the presence of ammonium thiocyanate in the solution, as has been shown by our experiments (Fig. 2, Curves 1 and 2).

In concentrated solutions of ammonium thiocyanate, the reduction of the complex of univalent copper takes place at potentials of the dropping mercury electrode from -0.52 to -0.72 V, while the concentration of the ammonium thiocyanate changes from 1.0 N to 6.0 N. In order decisively to confirm the fact that in the presence of comparatively concentrated solutions of ammonium thiocyanate only univalent copper exists in the solution, we carried out the following experiment. By reducing a solution of copper sulfate and sodium chloride with metallic copper, we prepared a chloride solution of univalent copper [3]. This synthesis took place in the absence of air. The solution obtained was transferred to an electrolyzer to have a polarogram made, and ammonium thiocyanate was there added. The polarogram of this solution coincided completely with the polarogram of the solution in which bivalent copper had been used as the original material (Fig. 2, Curves 3 and 4). In both cases, the half-wave copper potentials were the same for equal concentrations of the ammonium thiocyanate.

The dependence of the univalent copper current on the potential of the dropping mercury electrode is expressed by the equation of the polarographic wave:

$$\pi = \pi_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i},$$

where $\pi_{1/2}$ is the half-wave potential and i_d is the limiting diffusion current. For all the polarograms shown by us on the graph, using as coordinates π , the electrode potential, against $\log \frac{i}{i_d - i}$, the experimental values fall excellently on a straight line.

The tangent of the angle of inclination of the straight line corresponds to $\underline{n} = 1$.

This result is a satisfactory confirmation of the fact that the reduction of the univalent copper ions takes place on the dropping mercury electrode.

We arrive at the same results if we utilize for our calculation \underline{n} , the number of electrons which take part in the reduction of the copper ion, using the equation of Ilkovich.

$$i_d = 605 \quad n \quad D^{1/2} \pi^{1/2} t^{1/2} C.$$

Thus, there is no doubt that the ions of bivalent copper in a solution of ammonium thiocyanate are reduced to univalent ions. In order to determine the composition of the complex formed by the univalent copper with thiocyanate, we utilized the equation for the change in the half-wave potential during complex-formation in the solution:

$$(\pi_{1/2})_K - (\pi_{1/2})_2 = 0.059 \log K - p \cdot 0.059 \log C,$$

which in the coordinates $(\pi_{1/2})_K$ is a straight line.

From the graph (Fig. 3) the value of $p \cdot 0.059$ was equal to 0.240; this gives the value $p = 4$ for the coordination number. Consequently, the formula of the thiocyanate complex of univalent copper will be $\text{Cu}(\text{CNS})_4^{+}$.

A calculation of the instability constant of this complex with the formula given above led to the value $7 \cdot 10^{-10}$.

It follows from Table 2 that the half wave potential for the reduction of univalent copper does not depend on the temperature.

Thus, the temperature coefficient of the logarithm of the instability constant of the complex is close to zero, and this permits us to take the heat of formation of the complex from its ions as also close to zero.

SUMMARY

1. It has been determined that in the presence of ammonium thiocyanate, bivalent copper ions are reduced to univalent ions.
2. The reduction of univalent copper on the dropping mercury electrode from a solution containing thiocyanate ions takes place reversibly.
3. The coordination number of the thiocyanate complex of univalent copper, and its instability constant, have been found.

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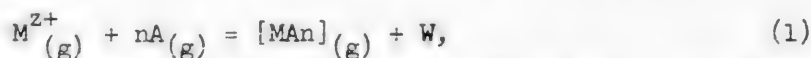
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December 27, 1948.

THE CLASSIFICATION OF COMPLEX FORMERS AND ADDENDS ON THE BASIS OF THEIR ENERGY CHARACTERISTICS

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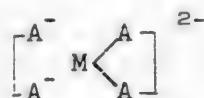
In order to judge the stability of complex ions, it is most expedient to review the process of formation of a gaseous complex ion from its constituent gas particles:



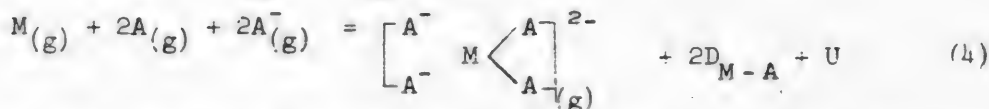
where M^{Z+} is the central ion, A is the addend, and $[MAN]$ is the complex ion. The change in energy during this process (W) we shall call "the energy of addition".

For complex ions with the predominant ionic type containing a chemical bond (aquo ions, complex fluorides, etc.), the energy of addition may be evaluated by means of the well-known equations of Kossel and Magnus. The value of W is determined in this case fundamentally by the electrostatic characteristics of the central ion and the addends (by the charges and radii of the ions, and for molecules, by the dipole moments).

In the case of complex ions with a covalent bond predominating (donor-acceptor) the energy of addition is not directly related to the electrostatic characteristics of the central ion and the addends. In order to evaluate the energy of addition in this case, we shall take as an example the formation of a complex ion with the structure:



according to the scheme above (1), we can break down the process into several steps:



Thus, for the energy of addition we obtain the following equation:

$$W = I - 2E + 2D_{M-A} + U. \quad (I)$$

where I is the total ionization potential, E is the electron affinity of the group A , D_{M-A} is the energy of the covalent bond $M-A$, and U is the resonance energy of the structure under consideration.

Generalizing Equation (1) for any covalent structure, we obtain.

$$W_c = I - nE + nD_M - A + U, \quad (II)$$

where n is the total number of donor-acceptor bonds in the complex ion.

The overall ionization potential of the central ion and the electronic affinity of the addend are decisive and make possible the quantitative calculation of the values involved in the formation of complex ions with predominantly covalent bonds.

There is also a very broad group of complex ions in which the essential role is played by the resonance of the ionic and covalent structures. The resonance energy attains a maximum value in the case where the energies of addition for the ionic and covalent structures are equal.

Working on this hypothesis, we can make a classification of complex ions and addends on the basis of their energy characteristics, and come close to an explanation of the phenomenon of selectivity during complex-formation. This phenomenon is pointed out by Grinberg, who paid attention to the fact that there is a definite relation between the nature of the complex-former and the addend, and that therefore it is impossible to speak about a tendency to complex-formation in general, without paying attention to the specific nature of the central atoms and the addends. Lebedinsky has indicated the possibility of dividing complex-formers into three groups, according to their tendency to form complexes with addends containing oxygen, nitrogen, and sulfur.

For the formation of a stable complex ion with a predominantly ionic bond, it is necessary not only that the central ion have a high charge and a small radius, but also that the addend have strong electrostatic characteristics (large charge and small radius, or considerable dipole moment). If at the same time the central ion is characterized by a comparatively low ionization potential, then it cannot form stable covalent complexes. Completely analogous are those addends which are characterized by a great electron affinity, and have no tendency to form stable covalent complexes. Thus, we can designate a group of central ions and of addends which we shall arbitrarily call "electrostatic". In this group we can place the ions with the outer shells of the inert gases, characterized by high charges and small radii (Be^{2+} , Al^{3+} , Ti^{4+} , Zr^{4+} , etc.). The corresponding addends will be F^- , H_2O , and in some cases CO_3^{2-} .

The central ions with high ionization potentials, but a low electrostatic characteristic, form stable complexes only with addends which have low electron affinities, as it follows from equation (II) that only when both these conditions are met simultaneously can the energy of addition attain an appreciable value. In this group we must place the ions with a non-inert gas nature of the last periods of the Mendeleev system (Au^+ , Hg^{2+} , Pb^{2+} , Bi^{3+} , Tl^+ , etc.). The specific

Note. Accepting the justified criticism of the so-called "theory" of resonance given by N. D. Sokolov (prog. chem. 18, 697 (1949)). I consider that the term "resonance energy" in my article is incorrect.

In this case we are speaking of the difference between the actual value of the energy of addition and that calculated by the method of additivity. The existence of this difference results from the fact that the actual bond in the ion $[\text{MA}]_2^+$ is intermediate between an ionic and a covalent bond, and it also results from the delocalization of the coordinate bonds.

The magnitude of this difference can be evaluated by means of a method of variations.

addends for this group of central ions will be $\text{S}_2\text{O}_3^{2-}$, I^- , CNS^- , Br^- , CSN_2H_4 , etc. In this case, too, the well-known selectivity will be observed, as the formation of stable complex ions with central ions or addends of the first group is improbable because of the low electrostatic characteristic of the particles of the group under consideration. The central ions and the addends of this group we shall arbitrarily call "covalent".

If the central ions are characterized by high ionization potentials and at the same time by large charges and small radii, they can form stable complexes with a large number of addends of different natures, and in particular with addends of both the first and second groups. Central ions of this type may be called "universal complex-formers". Typical representatives of this group are the multiply charged ions of the middle series of the transition groups of the Periodic System (Co^{3+} , Pt^{4+} , Ir^{3+} , Rh^{3+} , Cr^{3+} , Cu^{2+} , etc.).

In a completely similar way, we can also designate a group of "universal addends" which have at the same time both a high electrostatic characteristic and, apparently, a low electron affinity, as for example $\text{C}_2\text{O}_4^{2-}$, CN^- , $\text{C}_4\text{H}_4\text{O}_6^{2-}$, etc..

Finally, it is possible to have the case where neither electrostatic interaction alone, nor the formation of a donor-acceptor bond leads to a high value of the energy of addition, but as a result of the closeness of the values of the energy of addition for the ionic and covalent structures, a very great resonance energy arises. This sort of case probably exists with the singly-charged and doubly charged central ions of the subgroups of the Periodic System (Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Cu^+ , etc.). If the value of the ionization potential is at the same time large, complex-formation can take place with covalent addends as well (for example, for the ions Ag^+ , Cu^+ , Cd^{2+} , etc.). These "intermediate" addends apparently include the amines, ammonia, NO_2^- , HCO_2^- , etc. These addends can form stable complexes of ions not only with the intermediate central ions but also with the universal complex-formers. A summary of the main groups of complex-formers and addends is given in tabular form.

Name of group	Energy characteristics	Examples of complex formers	Examples of addends
1. Electrostatic complex-formers and addends	High charge, small radius, large dipole moment. Ionization potential comparatively low, electron affinity great.	Al^{3+} , Ti^{4+} , Zr^{4+} , Bi^{2+} , Hg^{2+}	F^- , H_2O , ROH , CO_3^{2-} , SO_4^{2-}
2. Covalent complex-formers and addends	High ionization potential, small electron affinity. Low electrostatic characteristics.	Au^+ , Hg^{2+} , Pb^{2+} , Bi^{3+} , Tl^+	$\text{S}_2\text{O}_3^{2-}$, I^- , CNS^- , Br^- , CSN_2H_4
3. Universal complex-formers and addends	High ionization potential, small electron affinity, high charge, and small ionic radius.	Co^{3+} , Pt^{4+} , Rh^{3+} , Ir^{3+} , Cr^{3+} , Cu^{2+}	$\text{C}_2\text{O}_4^{2-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, CN^-
4. Intermediate complex-formers and addends.	Average values of all energy characteristics.	Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} , Ag^+ , Cu^+ , Cd^{2+}	NH_3 , $\text{C}_2\text{H}_4(\text{NH}_2)_2$, NO_2^- , HCO_2^-

This classification is to an obvious degree conditional, in the sense that the boundaries set up between the different groups of complex-formers and addends just like the actual behavior of these or other particles, is determined by the calculated values of their fundamental energy parameters.

The structures given belong to the case where there is formation of gaseous

complex ions from gaseous constituent particles. In the formation of complex ions in solution, it is necessary to take into account in addition the fact that the molecules of solvent may also act as addends, forming complex solvions.

To a first approximation, for a definite group of complex ions, we can limit ourselves to a consideration of the differences between the energies of addition of the solvent molecules and of the given addends to the central ion, as the solvation effects for a given narrow group of complexes remains approximately constant (for example, within the group of amino compounds, complex chlorides, bromides, iodides, etc.).

In the formation of aquo-complexes, the decisive role is played by ionic dipole forces. In aqueous solutions with different energies of addition, the most stable complexes will be those with large central ions. Therefore, by no means all complex ions with high ionization potentials are capable of giving stable complexes with covalent addends in aqueous solutions. In this case, the most stable complexes will be those in which the central ion has large dimensions (Pb^{2+} , Ag^+ , Cd^{2+} , etc.) even if the ionization potential of such a central ion is lower than that of certain ions with small radii (for example, the Be^{2+} ion).

The large dipole moment of the H_2O molecules leads to the result that pure electrostatic complexes are seldom encountered in aqueous solutions. We may assume that in solvents with small dipole moments, electrostatic complexes will be characterized by great stability.

SUMMARY

On the basis of a review of energy characteristics, a classification is proposed for complex-forming and addend ions; according to this classification, both these and other particles are divided into four groups: a) electrostatic, b) covalent, c) universal, and d) intermediate (see table). An attempt is made from this point of view to explain the phenomenon of group selectivity during complex-formation and the differences in stability of the complex ions in solutions.

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THE PENTAAMMINOFORMATES OF COBALT (III)

K. B. Yatsimirsky

The cobalt pentamminoformates have been cited in the literature only once [1], and their synthesis requires a fairly complicated method. No data are given in the literature on the stability of these salts.

However, on the basis of the classification of complex-formers and addends [2] proposed by us, we can assume that the cobalt pentamminoformates will be fairly stable, and that therefore their synthesis too might be carried out in a more simple manner.

The Co^{3+} ion is characterized by a high charge, a small radius, and apparently a fairly high ionization potential, as a result of which it must be placed in the group of universal complex-formers [2]. As confirmation of this, there are the numerous and widely differing complex cobalt salts. On the basis of its energy characteristics, the formate ion (thermochemical radius 1.58 Å, electron affinity of the group HCO_2 75 kcal) may be placed in the group of intermediate addends, to a certain degree similar to NO_2^- (thermochemical radius 1.55 Å, electron affinity of NO_2 equal to 41 kcal). In connection with the high value of the electron affinity of the HCO_2 group as compared with that of the NO_2 group, we may consider that the pentamminoformates, being similar to the xanthates, will differ from the latter by their slightly lower stability.

Starting with the considerations just given, we decided to carry out a synthesis of the pentamminoformates of cobalt by a simpler method, and to study their thermochemical relations.

EXPERIMENTAL

The Synthesis of New Pentamminoformates of Co (III)

A 5 g sample of chloropentammino cobaltichloride was placed in a concentrated solution of potassium formate (100 ml) which contained approximately 8 times the amount of HCO_2K needed according to calculations based on the reaction:



The mixture obtained was heated almost to boiling during the time needed for complete solution of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (approximately 35 to 40 minutes). The red solution which was formed was cooled and mixed with an equal volume of a saturated solution of KI. Immediately upon mixing, red crystals of $[\text{Co}(\text{NH}_3)_5\text{HCO}_2]\text{Cl}_2$ precipitated.

The solution obtained was cooled to 0° , the precipitated crystals filtered off on a Buchner funnel with suction, and washed with ice water, aqueous alcohol,

and finally with 96% alcohol. The product obtained was dried in the air. The yield was 95% of the theoretical. Results of analysis:

	Calculated	Found
Cobalt	13.31%	13.45%
Iodine	57.30	57.25

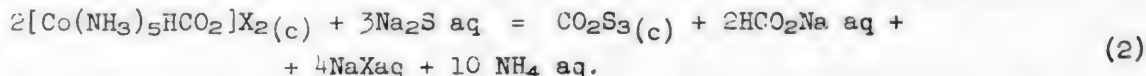
When to the solution obtained after boiling the solution of potassium formate, an equal volume of a solution of ammonium nitrate was added, intensely red crystals of $[\text{Co}(\text{NH}_3)_5\text{HCO}_2](\text{NO}_3)_2$ precipitated.

The preparation was treated further by the same method used for the pentaminoformate of cobaltiodide. Yield 90% of the theoretical.

Results of analysis: Cobalt: calculated 18.81%, found 18.69%; HCO_2^- : calculated 14.37%, found 14.52%.

The Thermochemistry of the Pentamminoformates of Cobalt (III) •

In order to determine the heats of formation of the two new complex salts we had synthesized, we measured the heats of reaction of the crystallized products with 0.26 mol. Na_2S solution. This took place according to the equation:



The heat of solution of both salts in water was also determined. All the measurements were carried out at 25°.

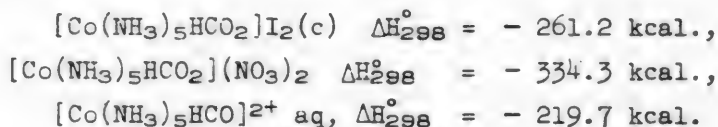
The apparatus and method of measurement have been previously described by us [6]. The results of the experiments are listed in Tables 1 and 2.

TABLE 1

The heats of reaction of the pentamminoformates of cobalt (III) with 0.26 mol Na_2S solution

Formula of salt	Weight, g	Change in temperature with correction for radiation	Correction for radiation	Heat capacity of calorimeter, cal.	Heat of reaction, cal.	Average value of heat, cal.
$[\text{Co}(\text{NH}_3)_5\text{HCO}_2]\text{I}_2$	1.0031	-0.013	+0.002	520.7	-2990	-3110
	0.9978	-0.014	+0.004	520.8	-3240	
$[\text{Co}(\text{NH}_3)_5\text{HCO}_2](\text{NO}_3)_2$	0.9989	0.028	0.000	520.7	-4570	-4560
	1.0000	0.028	+0.003	520.7	-4560	

Starting with the data obtained, we calculated the heat of formation of $[\text{Co}(\text{NH}_3)_5\text{HCO}_2]\text{I}_2$, $[\text{Co}(\text{NH}_3)_5\text{HCO}_2](\text{NO}_3)_2$, and the ion $[\text{Co}(\text{NH}_3)_5\text{HCO}_2]^{++}\text{aq}$. The heats of formation of all substances which took part in reaction (2) were taken from Bichowsky and Rossini's "Thermochemistry" [5]. This gave the following values for H° :



This section was done with L. L. Pankova.

TABLE 2

The heats of solution of pentamminoformates of cobalt (III) in water

Formula of salt	Weight (in g)	Dilution	Change in temp. (°C) with correction for radiation	Correction for radiation	Heat capacity of calorimeter (in cal.)	Heat of solution (in cal.)	Average value of heat of solution
[Co(NH ₃) ₅ HCO ₂]I ₂	0.6047	20330	-0.038	+0.002	529.2	-14730	14780
	0.5997	20500	-0.038	+0.002	529.0	-14840	
[Co(NH ₃) ₅ HCO ₂](NO ₃) ₂	0.6369	1246	-0.069	+0.002	528.9	-16400	16390
	0.6981	12447	-0.069	+0.003	529.1	-16380	

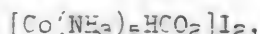
Consideration of Results

In order to obtain comparable results, it was necessary to calculate the energy of formation of the gaseous ion [Co(NH₃)₅HCO₂]²⁺, as only by doing this was it possible to avoid the influence of the surrounding ions and of the molecules of solvent on the stability of a given complex ion. The energy of formation of the gaseous complex ion could be calculated from the equation:

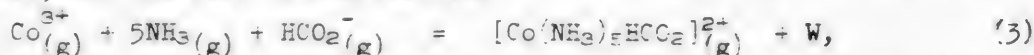
$$\Delta H_K = -\Delta H_A + \Delta H_{KA} - U_{KA} \quad (I)$$

where $-\Delta H_K$, $-\Delta H_A$, and $-\Delta H_{KA}$ were the heats of formation, respectively, of the gaseous cation, gaseous anion, and solid salt, and U_{KA} was the lattice energy of the complex salt. The latter value was calculated from Kapustinsky's equation on the assumption that the thermochemical radius of the [Co(NH₃)₅HCO₂]²⁺ ion was equal to 2.36 Å. This value was estimated from the fact that the difference between the heats of formation of the two salts mentioned was equal to the difference between the heats of formation of the corresponding chloropentammines. The thermochemical radius of the [Co(NH₃)₅Cl]²⁺ ion equaled 2.36 Å.

After substituting in Equation (I) the heat of formation of



the heat of formation of the gaseous ion [Co(NH₃)₅HCO₂]²⁺ was found to be equal to 194 kcal, and the heat of the reaction:



gave $X = 357$ kcal (X was the heat of formation of the gaseous ion Co^{3+}). A comparison of the values obtained for the heat of the reaction (3) with the heats of similar reactions for gaseous acido-pentamminocobalt ions led us to the conclusion that the thermal stability of the gaseous ion [Co(NH₃)₅HCO₂]²⁺ exceeded that of all the other ions studied with the exception of [Co(NH₃)₅NO]²⁺.

Thus, on the basis of a study of the thermal stability of the different gaseous acido-pentamminocobalt ions [6], we can construct the following series:



SUMMARY

1. Two new cobalt pentamminoformates have been synthesized by a very simple method. these are. [Co(NH₃)₅HCO₂]I₂ and [Co(NH₃)₅HCO₂](NO₃)₂.

2. The heats of reaction with a solution of sodium sulfide, the heats of solution, and the heats of formation of these salts have been determined.

3. It has been shown that the value of the energy of addition of the cobalt pentamminoformate ion is greater than that of the other acido-pentamminocobalt ions, with the exception of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$.

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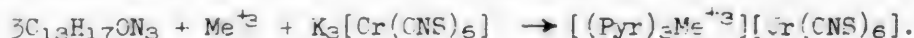
COMPLEX COMPOUNDS OF IRON ALUMINUM AND CHROMIUM WITH PYRAMIDON

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As the investigations of Gusev have shown, pyramidon reacts easily with acids of the type $H_2[Me(CNS)_6]$ [1]. The pyramidon complexes have two positions of coordination, as has been experimentally confirmed by Ryabchikov [2].

The action of pyramidon on solutions of the salts of trivalent metals (Fe, Al, Cr) in the presence of KNO_3 gives complex ions $Me^{+3}(Pyr)_3$, which are capable of substituting the cation of the outer sphere of the complex compounds of certain metals. Products have been obtained by reaction with the complex chromium thiocyanate $K_3[Cr(CNS)_6]$. The reaction takes place according to the equation:



The reaction results in forming a difficultly soluble double complex, which is in the form of an amorphous mass, which changes to a crystalline form. The formation of the precipitate takes place only in acid medium, while in neutral medium the precipitate does not form. Compounds were obtained with the composition $[(Pyr)_3Me][Cr(CNS)_6]$, where Me = Cr, Al, Fe (Fig. 1. See Plate, page 1591). In acetic acid medium, a compound of the composition $[(Pyr)_3H_3][Cr(CNS)_6]$ was obtained. This was a crystalline mass with a lilac color (Fig. 2. See Plate, page 1591). As a result of its insolubility, the precipitate could not be recrystallized.

Analysis of the compounds obtained

0.0712, 0.0838 g substance:	0.0052, 0.0066 g Cr_2O_3 .
0.1100, 0.1664 g substance:	0.0086, 0.0128 g Cr_2O_3 .
0.16, 0.05, 0.05 g substance:	0.1456, 0.0456, 0.045 g AgCNS.
Found %:	Cr 4.97, 5.38, 5.32, 5.24;
	CNS 31.83, 31.91, 31.78.
$[(Pyr)_3H_3][Cr(CNS)_6]$. Computed %:	Cr 4.7, CNS 31.8.
0.0984, 0.1504 g substance:	0.116, 0.018 g Cr_2O_3 .
0.1244, 0.1214 g substance:	0.1086, 0.105 g AgCNS.
Found %:	Cr 8.03, 8.15, CNS 30.40, 30.25.
$[(Pyr)_3Cr][Cr(CNS)_6]$. Computed %:	Cr 9.08; CNS 30.3.
0.1012, 0.06 g substance:	0.0914, 0.0538 g AgCNS.
Found %:	CNS 31.6, 31.35.
0.1102 g substance:	found by colorimetric method.
	% Al 1.4, 1.3.
$[(Pyr)_3Al][Cr(CNS)_6]$. Computed:	% Al 2.4, CNS 31.05.
0.1006 g substance:	Found % CNS 28.89, 29.0.
0.1278 g substance:	Found by colorimetric method
	% Fe 4.6, 4.6.
$[(Pyr)_3Fe][Cr(CNS)_6]$. Computed %:	Fe 4.95, CNS 30.2.

Pyr- $C_{13}H_{17}ON_3$ stands for pyramidon.

T A B L E

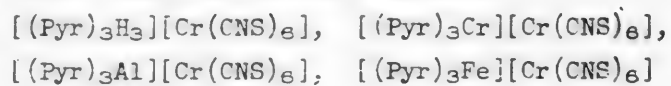
Property	$[(\text{Pyr})_3\text{H}_2][\text{Cr}(\text{CNS})_6]$	$[(\text{Pyr})_3\text{Cr}][\text{Cr}(\text{CNS})_6]$	$[(\text{Pyr})_3\text{Al}][\text{Cr}(\text{CNS})_6]$	$[(\text{Pyr})_3\text{Fe}][\text{Cr}(\text{CNS})_6]$
Color	Lilac	Grayish-lilac	Lilac	Brown
Solubility in 100 ml of water at 15°	0.07	0.08	0.07	0.108
Electrical conductivity	measurement unsuccessful			
Behavior with FeCl_3	No change in color	Color of solution orange - formation of $\text{Fe}(\text{CNS})_3$	Redish solution - formation of $\text{Fe}(\text{CNS})_3$	Brownish solution - formation of $\text{Fe}(\text{CNS})_3$
Behavior with NaOH in the cold	Dissolves, forming violet solution	Dissolves, to form violet-greenish solution	Dissolves to form violet solution	Dissolves, to form red solution
Behavior with NaOH upon heating	Forms precipitate of $\text{Cr}(\text{OH})_3$	Forms precipitate of $\text{Cr}(\text{OH})_3$	Forms cloud of $\text{Cr}(\text{OH})_3$	Solution with red color
Behavior with concentrated H_2SO_4	Dissolves, solution of yellow-green color	Dissolves to form dark-green solution	Dissolves to form light-green solution	Dissolves to form solution with yellow-green color
Behavior with conc. HNO_3	Dissolves with evolution of NO_2			
Behavior with HNO_3 (1 N solution) upon heating	Dissolves to form greenish solution			
Behavior with AgNO_3	Solution darkens, reduction to silver			
Behavior with $\text{HNO}_3 + \text{AgNO}_3$	Forms white precipitate			
Behavior with $\text{K}_4[\text{Fe}(\text{CN})_6]$	No change			Upon long standing forms bluish cloudiness
Upon heating above 50-60°	Decomposes with formation of vitreous mass			

The data obtained in this investigation made it possible to draw the following conclusions:

1. The trivalent metal elements Al^{3+} , Cr^{3+} , Fe^{3+} form complex compounds with a coordination number of 6 with organic amines.

2. The bond between the atom and the pyramidon is through the tertiary nitrogen atom on the one hand and the oxygen on the other. Thus, the molecule of pyramidon has two positions for coordination.

3. For the first time, the double complexes



have been obtained.

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THE NOMENCLATURE OF THE MOST IMPORTANT SILICO-ORGANIC COMPOUNDS

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It is well known [1-4] that of late there has been an increasing theoretical and practical knowledge of the elemento-organic compounds in general and of the silico-organic compounds in particular.

The practical application of these compounds had been predicted by numerous Russian and Soviet scholars who had conducted experimental and theoretical investigations, and had made a great historical contribution to the development of the chemistry of elemento-organic compounds [5,7].

In connection with the development of the chemistry and the chemical technology of silico-organic compounds, there arose the extremely important question of the nomenclature of silico-organic compounds. At present there is no single nomenclature of silico-organic compounds. The majority of names of silico-organic compounds proposed by different authors suffer from very serious failings. First of all they differ from each other, differ, in a number of cases, in length, have an accidental character, and most important, the names of many silico-organic compounds do not give a clear picture of their nature, do not express their visual qualities and their spatial arrangements.

As a result of these factors, many of the earlier names have already lost their significance:

The unsuitability of the nomenclature of silico-organic compounds becomes still more obvious as newer and newer silico-organic compounds are discovered, whose names cannot be fitted into the old terminology. As a result of all this, if the question under consideration of the nomenclature of silico-organic compounds has not yet been decisively confused, in any case, it has been considerably complicated.

In accordance with the old names, the silico-organic compounds which were derived from the simplest silane, SiH_4 , were named after the corresponding hydrocarbon derivatives of methane, with the addition of the prefix "silico". For instance $\text{Si}(\text{CH}_3)_4$ or $\text{C}_4\text{SiH}_{12}$ (in analogy with $\text{C}(\text{CH}_3)_4$ or C_4H_{10} , pentyldrane), was called silicopentyldrane, $(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$ or $\text{C}_6\text{SiH}_{14}$ (in analogy with $(\text{CH}_3)_2\text{C}(\text{C}_2\text{H}_5)_2$ or C_6H_{14} , heptyldrane) was called silicoheptyldrane. As a result of this, $(\text{CH}_3)_3\text{SiC}_2\text{H}_5$, in analogy with C_2H_6 , bore the same name as silicoheptyldrane $(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$.

The cause of this was to be found in the idea of the first investigators of silico-organic compounds, to the effect that there was a complete analogy between the compounds of silicon and the compounds of carbon. As a result, the first historical period of the silico-organic compounds, which lasted until the beginning of the twentieth century, was characterized by a tendency to identify

silico-organic compounds with the usual organic compounds. The formal similarity of some silico-organic compounds to their organic analogs strengthened this tendency. However, the experimental investigations of many scientists showed that the analogy between silicon and carbon compounds was a purely formal one, to be explained by the position of these elements in the same group of the Periodic System of D.I. Mendeleev [8].

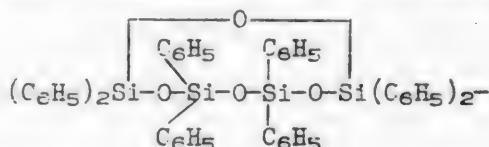
In 1905, Kipping [9,10] proposed his more rational terminology, which was adopted in England. On the basis of the terminology he proposed, we had: SiH_4 , which he called "silicane", and SiH_3OH , "silicanol". All the remaining compounds of silica were named from silicane and silicanol, as their derivatives. However, despite his own proposal to call hydroxyl-containing derivatives of hydrogen-silicone compounds "silicanols", Kipping himself often called them "silicols" (according to Ladenburg) [11].

In 1913, Martin [12] proposed that silico-organic compounds characterized by the -Si-Si- bond be called "silicoses", and those with the -Si-O-Si- bond "silicates". However, this suggestion never received widespread acceptance. [12]

In 1916, Stock published his nomenclature of silico-organic compounds, which was based on the names of the hydrogen-silicon compounds. He called the saturated hydrogen-silicon compounds silanes: SiH_4 was monosilane, Si_2H_6 disilane, Si_3H_8 trisilane, etc. [13]. Compounds which contained both silicon and carbon atoms at the same time were named by analogy with well-known compounds of carbon, with the addition of the prefix "silico"; those which did not contain carbon atoms were "persilico compounds".

For example, $\text{CH}_3\text{CH}_2\text{SiH}_3$ was monosilicopropane, Si_3H_8 was persilicopropane, etc.

Compounds which were characterized by the presence of alternating bonds of silicon and oxygen atoms were named siloxanes. For example;



was octaphenyltetrasiloxane.

Silicon compounds which differed in the content of oxygen and hydroxyl groups were to be designated, according to his recommendation, by using the prefixes "oxo" for oxygen and "hydroxy" for hydroxyl. For example,



was 1,3-bis-(hydroxy-oxo)-2,2-dihydroxytrisilane.

Stock's nomenclature obtained the widest acceptance, but it still suffered from essential deficiencies.

In 1944 Sauer [14] published an article on silico-organic terminology, as a member of an American commission for developing a rational nomenclature for silico-organic compounds [15].

The main differences between the nomenclature proposed by the American commission and that of Stock were the following:

- 1) Instead of the word "monosilane", "silane" was proposed.
- 2) Instead of the prefix "silico" to characterize silico-organic compounds, "sil" was proposed.

3) The names of silico-organic compounds which contained functional groups were to be constructed on the basis of the rules of genetic nomenclature of organic compounds.

4) New names were introduced for radicals which contained silicon, as for example:

According to Stock	According to Sauer
SiH_3 - monosilyl	silyl
Si_2H_5 - disilyl	disilanyl

etc.

We propose our nomenclature of silico-organic compounds based on the following considerations.

1. As the basis of our proposed nomenclature of silico-organic compounds we take the names of the corresponding hydrogen-silicon compounds, which are established in the Russian language; the atoms of these compounds are numbered from left to right.

For example:

SiH_4	silane
$\text{H}_3\text{Si}-\text{SiH}_3$	disilane
$\text{H}_2\text{Si}-\text{SiH}_2-\text{SiH}_3$	trisilane
$\text{H}_3\text{Si}-\text{SiH}_2-\text{SiH}_2-\text{SiH}_3$	tetrasilane
1 2 3 4	

If in a given silico-organic compound there is branching of the chain of atoms of the silicon, carbon, or any other element, then fundamentally the name of the silico-organic compound is included in a longer section of the straight silicon chain. In order to determine the position of the side chains or substituents, the number of the silicon atom where the side chain or substituent begins is indicated.

2. The presence of a hydroxyl group in a silico-organic compound (in accordance with the Geneva nomenclature) is indicated by the suffix "ol"; for example,

$(\text{CH}_3)_2\text{Si}(\text{OH})$	trimethylsilanol
$(\text{CH}_3)_2\text{SiH}-\text{SiH}_2-\text{SiH}_2\text{OH}$	1,1-dimethyltrisilan-3-ol.
1 2 3	

In the same way, the presence of an aldehyde, ketone, carboxyl group, etc., is signified by the suffixes "al", "one", "acid", etc.

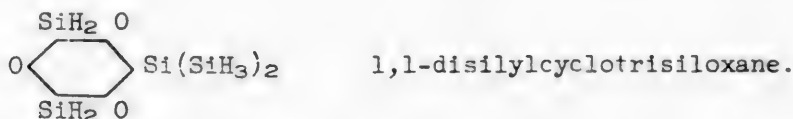
3. The presence of amino, nitro, alkoxy, and similar groups is indicated by the prefixes "amino", "nitro", "alkoxy", etc. For example:



4. The presence of different chemical elements in the composition of the silico-organic compound is shown by the corresponding name of the metal or non-metal, and indicated by the number of the silicon atom to which the given element is attached. For example,



5. Silico-organic compounds which are characterized by chains or rings, alternately attached to each other through atoms of silicon and oxygen, are called siloxanes. It might possibly be more correct to call these compounds "silanoxanes". However, (according to a suggestion by Prof. B.N. Dolgov) the former name is better. It is shorter, our chemists are already accustomed to it, and in addition, in the naming of complicated compounds, numerous uses of the suffix "an" in one and the same word will be avoided, as this suffix would give the idea that two or more saturated compounds are joined in the molecule. For example.



The proposed system of nomenclature in practice would encompass everything of theoretical and practical significance among the silico-organic compounds.

We may note the essential differences between our system of nomenclature and the systems proposed earlier by Ladenburg, Kipping, Martin, Stock, Sauer, etc.

1. The proposed names of silico-organic compounds give a clear understanding of their nature, and quickly summon the corresponding visual associations and spatial images of their structures, and do not suffer from unjustified lengthiness.

2. In contrast with the old nomenclature, this nomenclature is based on our contemporary ideas of silico-organic compounds.

3. The names of hydrogen-silicon compounds, which are at the basis of the proposed system of nomenclature of silico-organic compounds, are based on a system of terminology of the hydrogen-silicon compounds which has become established in the Russian language.

4. Instead of calling H_3SiOH "silicol" (according to Ladenburg), "silicanol" (according to Kipping), or "hydroxymonosilane" (according to Stock), we propose, in accordance with the Geneva nomenclature, "silanol".

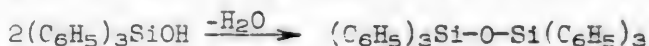
The number of hydroxyl groups or other substituents is indicated by the prefixes: 2, di; 3, tri; 4, tetra; 5, penta; 6, hexa, etc.

For example:



etc.

5. Instead of naming condensation products of silico-organic compounds which contain hydroxyls and react with the separation of water, as for example:



triphenylsilicanol oxide, or anhydrobistriphenylsilicanol (according to Kipping), we would keep the name "siloxanes". The above compound would therefore be called hexaphenyldisiloxane.

6. Instead of the name "silazanes" for nitrogen-containing silico-organic compounds of the type $\text{R}_3\text{SiNH}[\text{SiR}_2\text{NH}]_n\text{SiR}_3$, we propose the name silamines.

7. The names of silico-organic radicals would be built from the root of the corresponding hydrogen-silicon compounds. Thus, instead of calling the first member of the series, SiH_3 , "silicyl" (according to Kipping), "monosilicyl" (according to Stock), we would use the name "silyl", which is the name proposed by Sauer; but for the second member of this series, instead of the name of "disilyl" for Si_2H_5 (according to Stock), or "disilanyl" (according to Sauer), we would use "disil" (but not "disilyl", in order not to confuse the name of this radical with the designations of two "silyl" radicals), etc.

8. An understanding would be conveyed of silico-organic radicals, and in

A Comparison of Nomenclature for Silico-Organic Compounds

1478

particular, in place of

H_3SiO ... "siloxy" (according to Sauer) - "silyloxy";
 $H_3Si-SiH_2O$... "disilanoxy" (according to Sauer) - "disiloxy";
 $H_3Si-SiH_2NH$... "disilanylamino" (according to Sauer) - "disilamino", etc.

9. For silico-organic compounds which are polymerized products of the joining of silicon and bivalent radicals, we propose the names silanmethylenes, silanphenylenes, etc.

In order to compare our nomenclature with the terminology now used in various places, we provide a table, which demonstrates at a glance the advantages of the system proposed by us.

In conclusion, the author expresses his profound thanks to Prof. B.N. Dolgov, for his objective criticism of this work and his valuable suggestions, which were taken into account by the author in the final editing of this paper.

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THE VISCOSITY OF THE SYSTEMS FORMED BY BENZENE AND ITS HOMOLOGS WITH THE LOWER ALCOHOLS

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The viscosity of the system mesitylene-methyl alcohol was measured by us in connection with a study of the phenomenon of foam-formation in this system. During this, we obtained an unexpected, very characteristic, viscosity isotherm. This induced us to carry out similar measurements for a number of systems formed by methyl alcohol with the lower homologs of benzene (up to C_{10}). In the other direction, it appeared of interest also to compare the behavior of mesitylene in the system with methyl alcohol with its behavior in systems with other alcohols, and in particular, with ethyl and propyl alcohols.

In the literary sources we have searched we have found no data on the viscosity of these systems, except for the system benzene-methyl alcohol, which was studied at 25° and at the boiling points of the mixtures [1]. The 25° isotherm, which was calculated in both molar and volume percentages, appeared slightly convex to the axis of composition of the curve, very close to a horizontal straight line (the values of the viscosity for the components at this temperature were very close). The viscosity curves at the boiling points, obtained by A. Findley [2], passed through a maximum, which possibly resulted from the fact that the boiling points passed through a minimum.

Starting Materials and Method of Procedure

1. The methyl alcohol, which was used in a number of systems, was prepared from pure methanol by dehydration by means of long standing over calcined copper sulfate, and then boiling and distilling over calcium oxide. It distilled at the single point 64.5° at a pressure of 757 mm.
2. Chemically pure cryoscopic benzene was dried over metallic sodium and distilled within the limits 79.3-79.5° at 750 mm.
3. The toluene was also dried over metallic sodium and distilled in the narrow interval 110.0-110.1° at a pressure of 751 mm.
4. A pure preparation of *m*-xylol was dried over metallic sodium, and upon distillation went over within the limits 138.5-139.0° (pressure 758 mm).
5. Mesitylene was synthesized by us by the dehydration of acetone according to the well-known reaction:



As a result of the synthesis, after repeated distillation (over sodium) a fraction of pure mesitylene was collected which boiled at a pressure of 740 mm within the limits 163.0-163.6°.

6. A chemically pure preparation of p-cymene, after drying over metallic sodium, boiled at 176.2-176.4° (pressure 755 mm).

7. Ethyl alcohol was subjected to dehydration by the same treatment as the methyl alcohol. The fraction of absolute alcohol used in the work boiled completely at 78.0° at the atmospheric pressure of 748 mm.

8. Propyl alcohol (primary) was dried with calcium oxide and distilled over it. At a pressure of 745 mm it went over in the interval 96.4-97.2°.

All the compounds were tested for purity by measuring their density and comparing this with the data in the literature. The values of the density obtained by us are included in the tables for the corresponding systems. The density of the components and the mixtures was determined in a pycnometer with a volume of about 4 ml. All the weighing was carried out in vacuum. The viscosity was measured by means of an Ostwald viscosimeter, for which the time of flow of water amounted to about 3.5 minutes. All the measurements were carried out at a temperature of 20° (accuracy of thermostat-control $\pm 0.1^\circ$).

Results of Measurements

The values of the density and viscosity of the systems containing methyl alcohol are given in Tables 1 to 5. The data for the systems mesitylene-ethyl alcohol and mesitylene-propyl alcohol are arranged in Tables 6 and 7.

TABLE 1

Benzene-Methyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8788	0.646
2	10	0.8748	0.622
3	20	0.8694	0.613
4	40	0.8597	0.619
5	60	0.8432	0.626
6	80	0.8229	0.626
7	90	0.8094	0.610
8	100	0.7923	0.578

TABLE 2

Toluene - Methyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8660	0.593
2	20	0.8596	0.582
3	40	0.8517	0.601
4	60	0.8400	0.620
5	80	0.8223	0.623
6	100	0.7923	0.578

TABLE 3

m-Xylene - Methyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8656	0.627
2	20	0.8603	0.622
3	40	0.8524	0.636
4	50	0.8480	0.646
5	60	0.8412	0.662
6	70	0.8350	0.654
7	80	0.8264	0.641
8	100	0.7923	0.578

TABLE 4

Mesitylene - Methyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8626	0.705
2	20	0.8577	0.696
3	40	0.8531	0.699
4	50	0.8464	0.715
5	60	0.8401	0.721
6	80	0.8240	0.683
7	100	0.7923	0.578

The density isotherms of all these systems are curves convex to the axis of composition if the composition of the mixtures is expressed in molar percentages. As a function of the volume composition, the experimental values of the density in all cases fell fairly well on straight lines. This sort of relationship indicates

These two latter systems were investigated by one of us in the laboratory of Physical and Colloid Chemistry of the V. M. Molotov Rostov State University under the direction of Prof. N. A. Trifonov.

TABLE 5

p-Cymene - Methyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8560	0.826
2	20	0.8526	0.799
3	40	0.8467	0.793
4	60	0.8378	0.793
5	70	0.8315	0.774
6	80	0.8235	0.732
7	100	0.7923	0.578

TABLE 7

Mesitylene - n-Propyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8626	0.721
2	20	0.8577	0.748
3	40	0.8471	0.855
4	60	0.8371	1.075
5	80	0.8253	1.419
6	100	0.8050	2.102

that the systems under investigation are formed with practically no change in volume.

The viscosity curves of the systems with methyl alcohol have very characteristic shapes, which change in a regular manner from one system to the next.

They are compared in Fig. 1. They all have convex and concave portions, indicating deviations from the additivity values of the viscosity.

In all the systems, the positive deviations observed led to the formation of maxima. A maximum was absent only in the isotherm of the system with p-cymene; however, this was the result of the greater value of the viscosity of cymene in comparison with that of the lower homologs. The values of the maximal positive deviation from additivity decrease as the number of carbon atoms decreases, and in the case of toluene there is a small negative deviation, which becomes more appreciable in the system containing benzene. These observations are summarized in Table 8.

It is clear from Fig. 1 that the isotherms of systems with benzene have a special position among the other systems. This results in the anomaly already noted by Dunstan [6], including the fact that the viscosity coefficient of benzene is greater than that of toluene.

The unusual appearance of the viscosity isotherms of the systems containing methyl alcohol can be explained in the following manner. Associated molecules of methyl alcohol dissociate when they are dissolved in hydrocarbons, and lower the viscosity of the solution. Therefore the viscosity isotherms are lowered from the values of the ordinates of the pure hydrocarbons, leading, in the case of the lower homologs through a minimum and even below the straight line of additivity.

TABLE 6

Mesitylene - Ethyl Alcohol System

No.	CH ₃ OH, mol. %	d ₄ ²⁰	η_{20} , poises
1	0	0.8626	0.721
2	20	0.8548	0.718
3	40	0.8458	0.764
4	60	0.8343	0.854
5	80	0.8177	0.983
6	100	0.7903	1.181

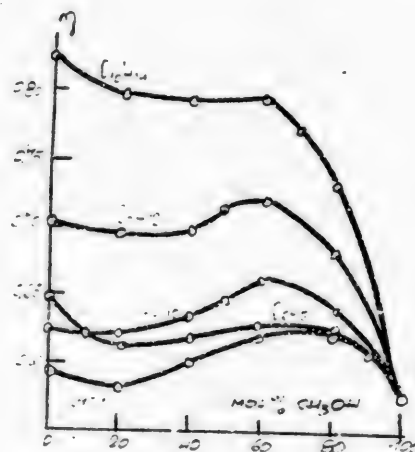


Fig. 1. Viscosity isotherms of the systems formed by benzene and its homologs with methyl alcohol.

TABLE 8

Deviations of the viscosity isotherms from additivity			
System	$\Delta\eta_{\max.}, \%$	CH ₃ OH, mol %	$\eta_{\text{addit.}}$
p-Cymene - methyl alcohol	+18.6	67	0.660
Mesitylene - methyl alcohol	+15.3	66	0.621
m-Xylene - methyl alcohol	+11.4	65	0.595
Toluene - methyl alcohol	- 0.7	16	0.590
	+ 7.3	75	0.580
Benzene - methyl alcohol	- 3.5	18	0.638
	+ 5.9	76	0.594

Dissociation is shown by the negative heat of mixing found for a number of the systems consisting of benzene or its homologs plus the lower alcohols; among these systems, the first two studied by us are included [7,10]. At higher concentrations another factor becomes more appreciable. This is the interaction between the components, or solvation.

Inasmuch as our measurements were carried out at only a single temperature, we did not use our data for the calculation of the value of the "energy bond" ϵ_{12} , according to the method of G.M.Panchenkov.[8] However, the path of the curves showed that this value could not be constant for the solutions. We must observe that in his theory of the viscosity of double liquid systems, G.M.Panchenkov does not foresee the case of isotherms which have simultaneously both a maximum and a minimum. Apparently our data either do not fit in with this theory or they indicate the fact that the systems studied must be referred to "Class II", i.e., they must be regarded as ternary, where the third component (whose concentration cannot be determined) is the solvate formed.

Thus, in our opinion, the complicated S-shaped course of the viscosity curves must be ascribed, on the one hand, to a decomposition of the associated methyl alcohol molecules, and on the other, to solvation in the solution.

The mutual imposition of these two effects also leads in all probability to the practically zero change in volume on mixing, already noted above. None the less, Mason and Paxton [5], on the basis of very accurate measurements of the density, still found that in the system toluene - methyl alcohol there was a slight compression, which at 25° did not exceed 0.12%. Washburn and Lightbody [9] also found that in the system benzene - methyl alcohol there was a small amount of compression in the region of high alcohol concentrations, and that, on the other hand, there was expansion at low alcohol concentrations. These phenomena are ascribed to the processes of solvation and dissociation respectively. It is characteristic that according to

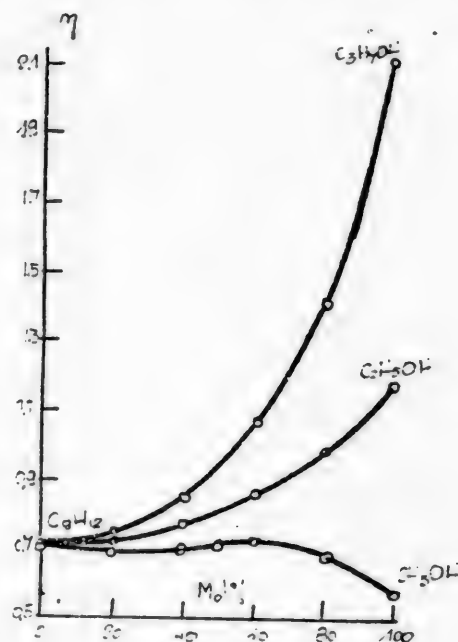


Fig. 2. Viscosity isotherms of the systems formed by mesitylene with the lower alcohols.

the data of the same authors [9], the isotherms of the systems formed by benzene and toluene with ethyl alcohol have the same appearance. Thus, while in the system toluene - methyl alcohol no expansion is observed (at normal temperatures), in the similar systems with ethyl alcohol it definitely exists. Apparently, in this case the phenomenon of dissociation plays a greater role than in the system with methyl alcohol. We can expect this to a still greater degree in the case of propyl alcohol.

We can arrive at the same conclusion on the basis of a study of the viscosity of the systems containing mesitylene, (Fig. 2).

In the systems formed by mesitylene with ethyl and propyl alcohols, the course of the viscosity isotherms is different from those described above. This is the ordinary type of diagram for systems which contain associated liquids. Apparently, in these systems the effect of solvation is weaker, and the considerable association of the molecules of the alcohols, which are much more viscous than mesitylene, leads to our obtaining curves which are concave over their entire course.

SUMMARY

1. The values of the viscosity (and density) have been measured at 20° for systems which contain methyl alcohol with benzene, toluene, m-xylene, mesitylene, and p-cymene, as well as for mesitylene with ethyl and with n-propyl alcohols.

2. The viscosity isotherms of the first five systems are convex to the axis of composition in the region of low concentrations and concave to it at high concentrations of alcohol. In a number of cases, minima and maxima are observed on them.

3. The isotherms of the last two systems are convex to the axis of composition throughout their entire length.

4. An explanation is proposed for the peculiar shapes of the curves. This is to be found in the dissociation of associated molecules of alcohol and solvation in solution.

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THE ALKYLATION OF ACYL DERIVATIVES OF AROMATIC AMINES

BY THE FRIEDEL CRAFTS REACTION

2 THE ALKYLATION OF ACETANILIDE

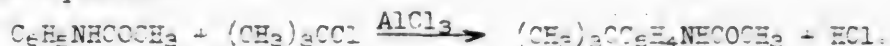
G. S. Kolesnikov and T. V. Smirnova

The Mendeleev Moscow Chemical Technological Institute, awarded the Order of Lenin

In a continuation of a previously begun investigation [1], we attempted to alkylate acetanilide by means of various alkylating agents. The alkylation was carried out both under conditions described in the previous communication and under conditions indicated in the patent literature [2]. As alkylating agents we used: methyl iodide, ethyl bromide, n-propyl bromide, n-butyl bromide, tert. butyl chloride, and the ethyl ester of chlorocarbonic acid, which in the presence of aluminum chloride ethylates aromatic compounds [3].

When the alkylation reaction was carried out under the conditions indicated in patents (in a dichloroethane medium at a temperature from -5 to -10°) with different durations of the experiments (from 30 minutes to 6 hours) it was found that the reaction did not take place in even one case, and after treatment of the reaction mixture, the original acetanilide was recovered almost quantitatively. When more stringent conditions were used for alkylation, as established by us during the alkylation of acetanilide with isobutyl bromide in the presence of aluminum chloride [4], it was found that the alkylation of acetanilide took place only under the action of tert. butyl chloride. The use of the other alkylating substances mentioned above was unsuccessful, and the acetanilide used for the reaction was recovered almost quantitatively. The alkylation of acetanilide with tert. butyl chloride took place under these conditions fairly slowly, and the yield of p-tert. butylacetanilide was small. Only when more stringent conditions were used, in particular when the temperature of the reaction was raised to $100-102^{\circ}$ and the heating was continued for three hours did the yield of p-tert. butylacetanilide become satisfactory. It amounted to 75% of theory, basing the calculation on the acetanilide which had reacted, or to 62%, basing the calculation on the acetanilide used for the reaction.

The formation of p-tert. butylacetanilide can be indicated in its overall aspect by the equation:



It is of interest to note that the use of isobutyl bromide [5] and tert. butyl chloride as alkylating agents leads to the formation of one and the same product - p-tert. butylacetanilide. This fact permits us to make certain assumptions about the mechanism of the alkylation of acetanilide in the nucleus by means of isobutyl bromide in the presence of aluminum chloride.

The first stage of the reaction is apparently the formation of a complex compound of acetanilide with aluminum chloride.

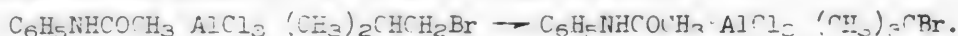


It is known that compounds which contain the carbonyl group easily form complexes with aluminum chloride [4]. The complex compounds formed react with the alkylating agent, the isobutyl bromide, to give a triple complex:



The existence of triple complexes of aluminum chloride, an aromatic compound, and an alkyl halide has been shown by Norris [5].

The next stage in the reaction appears to be the conversion of the isobutyl bromide into tert. butyl bromide inside the triple complex. It is known that isobutyl bromide and isobutyl iodide easily isomerize into tert. butyl bromide and iodide even upon heating [6], isomerization takes place more easily in the presence of aluminum chloride. The conditions under which the experiment is carried out (increased temperature and the presence of aluminum chloride) are entirely favorable to the possibility of such isomerization:



The interaction of the tert. butyl bromide formed with acetanilide inside the triple complex leads to the formation of a complex compound of tert. butyl acetanilide, aluminum chloride, and hydrogen bromide:



Under the conditions in which the reaction is carried out, this complex compound is decomposed with the evolution of hydrogen halide, which consists of a mixture of hydrogen chloride and bromide, in accordance with observations previously made [7]; the content of hydrogen chloride and bromide in this mixture was not determined.



Consequently, the formation of tert. butylacetanilide by the action of butyl bromide is the result of its isomerization to give tert. butyl bromide. The absence of reaction between the acetanilide and ethyl bromide, n-propyl bromide, n-butyl bromide, methyl iodide, and the ethyl chloride which is formed by the decomposition of the ethyl ester of chlorocarbonic acid in the presence of aluminum chloride, permits us to assume that in order for the alkylation of acetanilide to take place in the nucleus in the presence of aluminum chloride, tertiary alkyl halides must be used, or alkyl halides which are capable under the conditions of the reaction of isomerizing to give tertiary alkyl halides. The alkyl halides enumerated above are not tertiary, and their isomerization does not lead to the formation of tertiary alkyl halides.

EXPERIMENTAL

The Alkylation of Acetanilide with Tert. Butyl Chloride

In a three-necked flask fitted with a reflux condenser, a dropping funnel, and a mercury-seal stirrer, there were placed 150 ml of symm. tetrachloroethane, 34 g (0.25 mole) of acetanilide, and 40 g (0.30 mole) of aluminum chloride. The mixture was heated on the water bath at 60° while being stirred until the formation of a uniform solution, and it was then cooled to room temperature. To the cooled solution there was added drop by drop, with stirring, 27 g (0.29 mole) of tert. butyl chloride. The mixture was heated to 55-60° and maintained at this temperature for 50 minutes, after which the temperature was raised to 100-102° (the bath contained salt solution) and the reaction mixture was maintained at this temperature for three hours. After this the contents of the flask were cooled and decomposed by pouring into a dilute solution of hydrochloric acid (1:2). The tetrachloroethane layer was removed, washed with water, and transferred to a flask with 250 ml of 30% sulfuric acid. The mixture was distilled with steam until

there was no more distillation of the tetrachloroethane. The residue was made alkaline with caustic alkali and steam distillation was continued, the distillate collected being kept separate from the preceding one. The free amines were extracted from this distillate with ether, and the ether solution was dried with caustic potash and the ether driven off. From the residue, products which boiled up to 194° were distilled. The distillate, which boiled chiefly from 182 to 188°, weighed 5 g. After treatment with acetic anhydride it gave acetanilide, identified by us by its melting point, and by the absence of a lowering of the melting point when mixed with acetanilide. The residue from the distillation weighed 8.5 g, and after treatment with acetic anhydride gave 9.7 g of a substance which after repeated recrystallization from dilute alcohol melted at 167-169° and gave no depression of the melting point when mixed with p-tert. butylacetanilide.

After the distillation, there remained in the flask 20 g of solid material. After repeated recrystallization from dilute alcohol, this melted at 168-169°, and gave no lowering of the melting point when mixed with p-tert. butylacetanilide; this indicated the identity of this substance with p-tert. butylacetanilide. The total yield of p-tert. butylacetanilide was thus 29.7 g, which amounted to 76% based on the acetanilide which had reacted or 62% based on the acetanilide used in the reaction.

SUMMARY

1. It has been found that acetanilide is not alkylated by methyl iodide, ethyl bromide, n-propyl bromide, n-butyl bromide, and the ethyl ester of chloro-carbonic acid in the presence of anhydrous aluminum chloride.
2. The reaction of acetanilide with tert butyl chloride in the presence of aluminum chloride leads to the formation of p-tert. butyl acetanilide.
3. Opinions have been expressed with regard to the mechanism of alkylation of the acetanilide.

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DERIVATIVES OF ACETYLENE

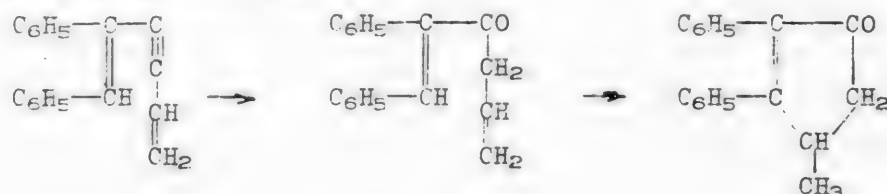
114 THE MECHANISM OF HYDRATION AND CYCLIZATION OF THE DIENINES

XXIII. The Synthesis of 1,2-Di-(p-hydroxyphenyl)-3-Methyl $\Delta^1,2$ -Cyclopentene-5-one by the Method of Hydration and Cyclization of the Dienines

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Institute of Organic Chemistry of the Academy of Sciences of the USSR

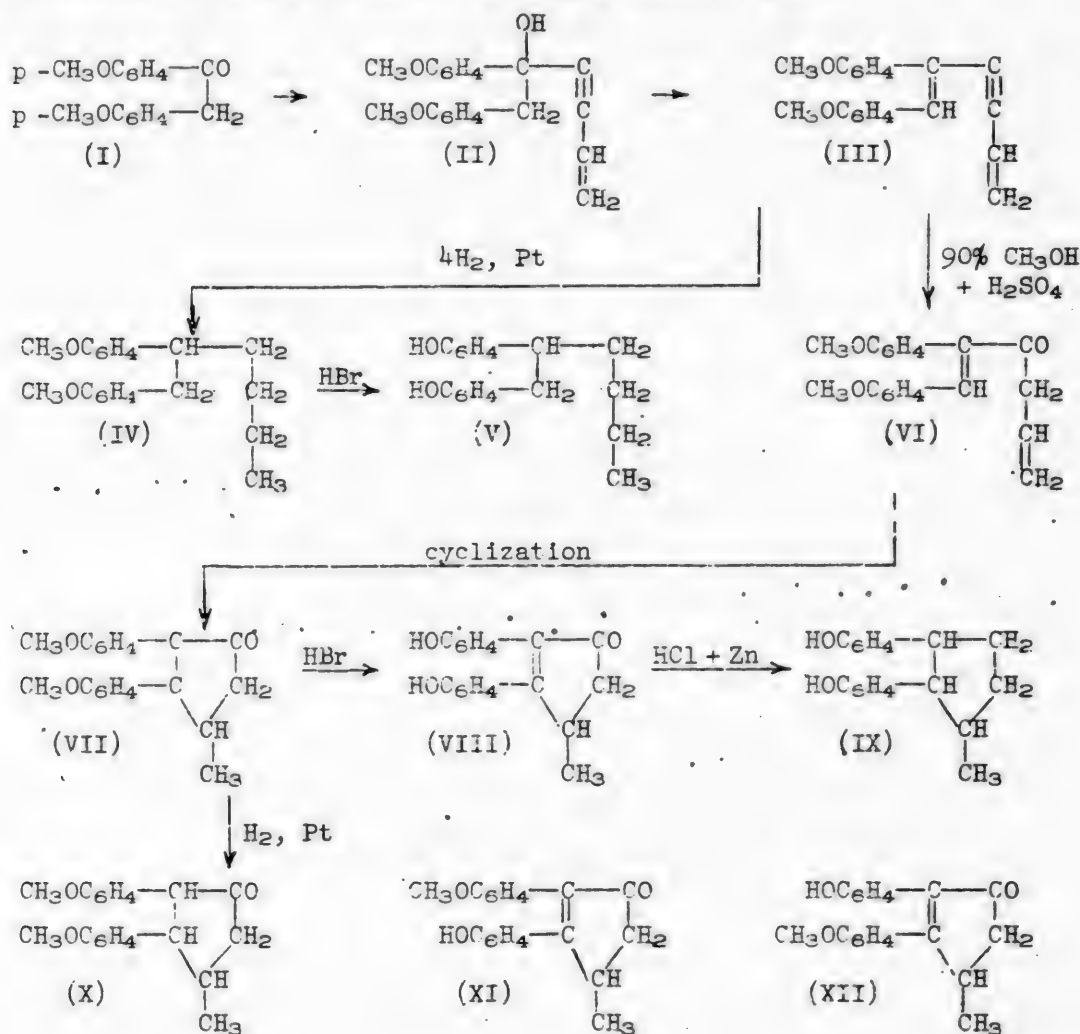
In preceding articles we [1,2] have shown that dienines which contain aromatic radicals can be hydrated and cyclized to give the corresponding cyclopentenones in the same way as the dienines of the aliphatic and alicyclic series. Thus, for example, it has been shown [2] that 5,6-diphenyl-1,5-hexadiene-3-ine is easily hydrated in aqueous solutions of methanol in the presence of sulfuric acid and mercury sulfate to 5,6-diphenyl-1,5-hexadiene-4-one, and that the latter, under the influence of phosphoric acid is quantitatively cyclized to give 1,2-diphenyl-3-methyl- $\Delta^1,2$ -cyclopentene-5-one:



Thus, the reactions of hydration and cyclization of the dienines which have been discovered in our laboratory can be successfully applied to the synthesis of various cyclopentenones containing not only aliphatic but also aromatic substituents. It was of interest to apply this method also to the synthesis of cyclopentenones containing p-hydroxyphenyl radicals.

As the starting material for these syntheses we used desoxyanisoin (I), upon which vinylacetylenyl magnesium bromide acted to give p-methoxyphenyl-p-methoxybenzyl-vinylethynyl carbinol (II) in more than 90% yield. This carbinol, however, was not isolated in pure form, as upon distillation even in a vacuum of 0.06 mm it decomposed to give vinyl acetylene and the original desoxyanisoin. The carbinol (II), like the other aromatic vinylethynyl carbinols, was extremely easily dehydrated in the presence of traces of acid reagents, to give an almost quantitative yield of 5,6-di-(p-methoxyphenyl)-1,5-hexadien-3-ine (III). Upon hydrogenation of the dienine (III) with Pt catalyst in a solution of glacial acetic acid, 4 molecules of hydrogen were absorbed and 5,6-di-(p-methoxyphenyl)-hexane (IV) was formed. This was then demethylated by means of hydrobromic acid to give 5,6-di-(p-hydroxyphenyl)-hexane (V). Upon heating the dienine (III) in aqueous solutions of methanol, in the presence of sulfuric acid and mercuric sulfate, 5,6-di-(p-methoxyphenyl)-1,5-hexadiene-4-one (VI) was formed in good yield. Even under the conditions of this reaction it was cyclized to give 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^1,2$ -cyclopenten-5-one (VII).

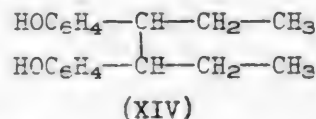
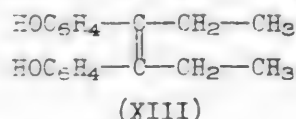
When the cyclopentenone (VII) was demethylated by means of concentrated hydrobromic acid in a solution of glacial acetic acid, 1,2-di-(p-hydroxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopentene-5-one (VIII) was obtained in 75% yield. By more careful demethylation of the cyclopentenone (VII) the cyclopentenone (XI) or (XII) was also obtained, with a content of a single methoxyl group.



Upon reducing the cyclopentenone (VIII) by the Clemmensen method, 1-methyl-2,3-di-(p-hydroxyphenyl)-cyclopentane (IX) was formed, obtained in the form of a very viscous mass, as distinguished from all the other products described above, which were well-crystallized substances. As has been noted previously more than once, the catalytic hydrogenation of the cyclopentenones which have two substituents attached to the ring double bond (especially aromatic or heavy aliphatic substituents) takes place under ordinary conditions very slowly, as a result of the screening influence of these substituents on the double bond (steric hindrance). Usually the hydrogenation of such cyclopentenones in the presence of Pt catalyst in alcohol solution does not take place at all, and it is therefore carried out in a solution of glacial acetic acid. Under these conditions the cyclopentenone (VII) can also be hydrogenated to give the cyclopentanone (X). We must note that 1,2-diphenyl-3-methyl- $\Delta^{1,2}$ -cyclopentene-5-one, as has been shown by us in one of the preceding communications [2], is completely incapable of being hydrogenated in the presence of Pt catalyst at room temperature, and this hydrogenation was

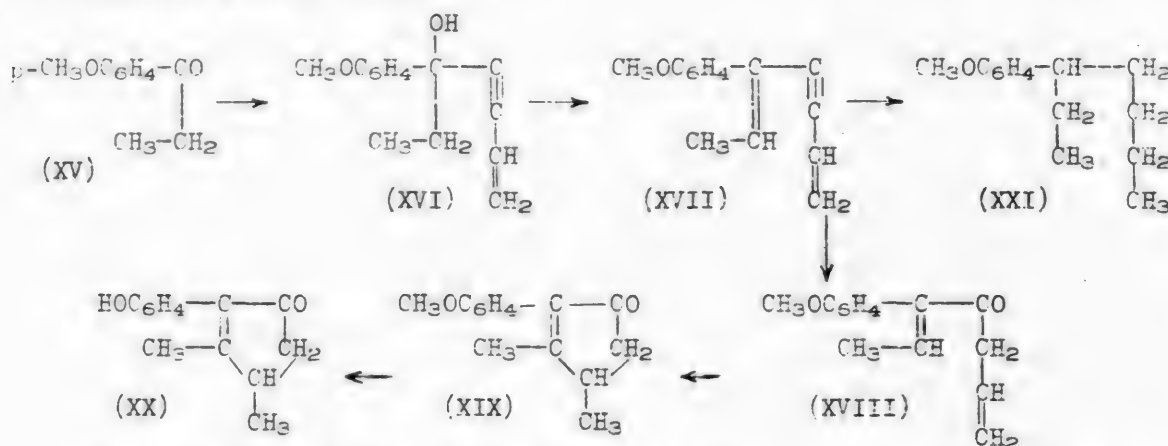
carried out only at a temperature of 100°. Consequently, the introduction of methoxyl groups into the aromatic nucleus considerably facilitates the hydrogenation of the double bond in the cyclopentenone (VII).

The compounds (VIII) and (IX), which were synthesized by us, may be regarded as cyclic analogs of stilbestrol (XIII) and hexestrol (XIV), which have, as is well known, remarkably high estrogenic activity [3]:



However, the compounds (VII), (VIII), and (IX), when tested on infantile mice in doses up to 100 γ showed no estrogenic activity. This may be explained by the cis configuration of these compounds [4]. It is known that the great biological activity of stilbestrol, as well as of the natural steroid hormones, is related to the trans configuration of these compounds.

By the method of hydration and cyclization of dienines we also synthesized the cyclopentenone (XX), which contains only a single p-hydroxyphenyl radical. As the starting material for this synthesis we used p-methoxypropiophenone (XV), upon which vinylacetylenyl magnesium bromide acted to give ethyl-p-methoxyphenyl-vinylethynyl carbinol (XVI), the latter being dehydrated to give 5-p-methoxyphenyl-1,5-heptadiene-3-ine (XVII).



Upon hydrogenating the dienine (XVII) in the presence of Pt catalyst in a solution of methanol, 4 molecules of hydrogen were absorbed and 5-methoxyphenylheptane (XXI) was obtained. When the dienine (XVII) was hydrated in aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate, a high yield of 5-p-methoxyphenyl-1,5-heptadiene-4-one (XVIII) was obtained. Even under the conditions of the reaction this was partially cyclized to give 1-p-methoxyphenyl-2,3-dimethyl- $\Delta^{1,2}$ -cyclopentene-5-one (XIX). The cyclization of the dienone (XVIII) to give the cyclopentenone (XIX) took place completely upon heating to 150-155° in the presence of 0.1% of p-toluenesulfonic acid for a period of 10 to 15 minutes. Demethylation of the cyclopentenone (XIX) by means of hydrobromic acid in a solution of glacial acetic acid gave 1-p-hydroxyphenyl-2,3-dimethyl- $\Delta^{1,2}$ -cyclopenten-5-one (XX). Hydrogenation of the cyclopentenone (XIX) in the presence of Pt catalyst at room temperature took place extremely slowly even in a solution of glacial acetic acid, and could not be completed under these conditions.

EXPERIMENTAL

The preparation of anisoin. A mixture of 80 g of anisoin aldehyde, 92 ml of alcohol, 52 ml of water, and 16 g of potassium cyanide was stirred at a bath

temperature of 105° for 2 hours. Then 16 additional g of potassium cyanide were added, and the stirring was again continued for 3 hours. After the solution had been cooled, the precipitated potassium cyanide was filtered off, and the filtrate was allowed to stand in a vacuum to remove the alcohol. During this process, a precipitate of anisoin formed, and after 15 minutes the mixture almost solidified. The anisoin was filtered off in vacuum and washed on the filter with 40% alcohol until the wash liquid remained colorless. After recrystallization from 50% alcohol, 38 g of anisoin were obtained, which melted at 112-113°. The filtrate was diluted with water, and a heavy dark-yellow oil precipitated out. This was dissolved in 35 ml of alcohol, and to the solution there were added 12 ml of water and 6 g of potassium cyanide. The reaction mixture was stirred for 6 hours at a bath temperature of 105°. After treatment in a manner similar to the preceding, an additional 13.5 g of anisoin was obtained. Thus, from 80 g of anisic aldehyde, 51.5 g of anisoin was obtained [5].

The reduction of anisoin to desoxyanisoin. To a mixture of 50 g of anisoin and 128 g of hydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) there were added 120 ml of concentrated hydrochloric acid and 125 ml of alcohol. The mixture was heated on the boiling water bath for 2 hours with vigorous stirring, and then poured into 500 ml of 5% hydrochloric acid. The desoxyanisoin which precipitated out after cooling was filtered and washed with water until there was no more acid in the wash water. After recrystallization from petroleum ether, 47 g of desoxyanisoin (I) was obtained; it melted at 109-110° [6].

The synthesis of p-methoxyphenyl-p-methoxybenzyl-vinylethynyl carbinol. To an ether solution of vinylacetylenyl magnesium bromide prepared from 24 g of magnesium, 115 g of ethyl bromide, 600 ml of ether, and 100 g of vinylacetylene, there was added over a period of 10 minutes, with vigorous stirring, 74 g of desoxyanisoin (m.p. 109-110°). The reaction mixture was stirred at 35-40° for 2 hours, then allowed to stand for 12 hours at room temperature, and after 2 hours of heating at 40-50° was carefully hydrolyzed by means of 350 ml of 10% hydrochloric acid at a temperature of 20°. The product was extracted with ether, washed with a solution of sodium bicarbonate, and dried with potash. After the ether had been driven off in vacuum, 85 g of an extremely viscous syrupy dark-yellow liquid was obtained. This was crude p-methoxyphenyl-p-methoxybenzyl-vinylethynyl carbinol (II). When an attempt was made to distill 1 g of the carbinol in a vacuum of 0.06 mm in the presence of hydroquinone, it decomposed to give vinylacetylene and desoxyanisoin.

The dehydration of p-methoxyphenyl-p-methoxybenzylvinylethynyl carbinol.

a) 60 g of the raw carbinol (II) was diluted to twice the volume with ether, 1 drop of 10% hydrochloric acid was added to the solution, and the ether was slowly driven off on the water bath, whose temperature by the end of the distillation had risen to 80°. On the surface of the liquid there appeared an aqueous layer. After all the ether had been driven off, the reaction mixture was cooled. It crystallized completely. The crystalline product was recrystallized from 90% methanol. 50 g of 5,6-di-(p-methoxyphenyl)-1,5-hexadien-3-ine (III) was obtained in the form of light-yellow needles which melted at 84°.

b) 13.2 g of the crude carbinol (II) was mixed with 30 mg of p-toluenesulfonic acid. The reaction mixture was heated for 40 minutes in a vacuum of 20 mm at 100°, until there was no more evolution of water. After the residue had been cooled in the flask, it crystallized. Recrystallization from 90% alcohol gave 12 g of the dienine (III) in the form of light yellow silky needles which melted at 84°, and dissolved easily in hot and with great difficulty in cold alcohol.

5.080 mg substance. 15.387 mg CO_2 , 2.880 mg H_2O .

3.925 mg substance. 11.900 mg CO_2 , 2.200 mg H_2O .

Found %: C 82.66, 82.74; H 6.34, 6.27.

$\text{C}_{20}\text{H}_{18}\text{O}_2$. Computed %: C 82.65; H 6.21.

The hydrogenation of 5,6-di-(p-methoxyphenyl)-1,5-hexadien-3-ine. 1.9 g of the dienine (III) was hydrogenated with Pt catalyst in a solution of 30 ml of glacial acetic acid. Over a period of 6 hours, 600 ml of hydrogen were absorbed, 500 ml of this being absorbed in one and a half hours. After the acetic acid had been driven off, the substance was distilled in vacuum. 1.8 g of 5,6-di-(p-methoxyphenyl)-hexane (IV) was obtained in the form of a colorless viscous liquid.

B.p. 174-175° at 1 mm; n_D^{14} 1.5429; d_4^{20} 1.018; MR_D found 89.9.
computed 90.56.

5.420 mg substance. 15.947 mg CO_2 , 4.287 mg H_2O .

Found %: C 80.29; H 8.85.

$C_{20}H_{26}O_2$. Computed %: C 80.40; H 8.72.

The demethylation of 5,6-di-(p-methoxyphenyl)-hexane. 1.2 g of the substance (IV) was dissolved in a mixture of 20 ml of glacial acetic acid and 10 ml of hydrobromic acid which had been saturated at 23°. The mixture was heated at 120° for 2.5 hours. The acid was driven off in vacuum by means of a water-jet pump, and the substance dissolved in 50 ml of 3% caustic soda. In order to remove the neutral products from the alkali, the solution was treated three times with ether, acidified with hydrochloric acid, and the product extracted with ether and dried over magnesium sulfate. After the ether had been driven off, the substance was distilled in vacuum. 1 g of 5,6-di-(p-hydroxyphenyl)-hexane (V) was obtained. B.p. 212-215° at 0.1 mm. The substance was a light-yellow extremely viscous oil, which after 2 days crystallized to give a light-yellow crystalline mass which melted at 74-75°.

5.570 mg substance. 16.325 mg CO_2 , 4.195 mg H_2O .

Found %: C 79.98; H 8.43.

$C_{18}H_{22}O_2$. Computed %: C 79.85; H 8.14.

The hydration and cyclization of 5,6-di-(p-methoxyphenyl)-1,5-hexadien-3-ine. a) 1 ml of concentrated sulfuric acid was dissolved in 40 ml of 90% methanol, and to the solution there was added 0.9 g of mercuric sulfate, and 2 g of the dienine (III). The mixture was stirred at a temperature of 60° for 2.5 hours. The product was diluted with water (70 ml). The partially crystallized oil which separated out was removed and heated for 15 minutes at 100° with 3 ml of phosphoric acid (sp. gr. 1.78). In order to remove the phosphoric acid, the reaction mixture was boiled twice for 15 minute periods with 50 ml of water. The solid reaction product was then squeezed between sheets of filter paper and heated at 100° in the vacuum of a water-jet pump. After this the substance was distilled in a high vacuum. 1 g of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VII) was obtained. B.p. 229-230° at 0.067 mm. M.p. 134° (from gasoline).

b) A mixture of 300 ml of 90% methanol, 6 ml of concentrated sulfuric acid, 2 g of mercuric sulfate, and 30 g of the dienine (III) were stirred for 3 hours at 65°. One hour and 2 hours after the beginning of the reaction, 2 g portions of mercuric sulfate were added. At the end of the reaction the solution was diluted with water (400 ml), and the oil and crystals which settled on the bottom were separated and washed with ether. This gave 13 g of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VII), with m.p. 134°. It gave no depression of the melting point with the sample described above, obtained in experiment (a). The viscous oil obtained after distilling the ether contained the dienone (VI). It was heated in a vacuum of 16 mm for 20 minutes at 180° with 0.05 g of p-toluenesulfonic acid. Upon cooling, the reaction mixture crystallized. The product was crushed, extracted with ether, and recrystallized from benzene. An additional 10 g of the cyclopentenone (VII) was obtained, with m.p. 134°. Thus, this experiment gave a total of 23 g of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VII).

c) 150 ml of 90% methanol, 5 ml of concentrated sulfuric acid, 1 g of mercuric sulfate, and 11 g of the dienine (III) were stirred at 65° for 6 hours. During this time a crystalline precipitate with a black color formed. The water was removed by decantation, and the precipitate was washed with ether. After recrystallization from gasoline (boiling range 50 to 110°) 7 g of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VII) were obtained in the form of light-yellow lustrous crystals which melted at 134°.

3.130 mg substance. 9.017 mg CO₂; 1.918 mg H₂O.
 5.809 mg substance. 16.624 mg CO₂; 3.440 mg H₂O.
 Found %: C 78.56, 78.08; H 6.85, 6.62.
 C₂₀H₂₀O₃. Computed %: C 77.85; H 6.49.
 Found %: OCH₃ 20.7 (Tseizel).
 C₂₀H₂₀O₃. Computed %: OCH₃ 20.1.

The oxime of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one was obtained in the form of white crystals, m.p. 185° (from alcohol).

6.210 mg substance. 0.253 ml N₂ (22°, 751 mm).
 6.170 mg substance. 0.242 ml N₂ (20°, 753 mm).
 Found %: N 4.65, 4.52.
 C₂₀H₂₁O₃N. Computed %: N 4.33.

The hydrogenation of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one. 4.9 g of the cyclopentenone (VII) were hydrogenated with Pt catalyst in a solution of 20 ml of glacial acetic acid. The hydrogen was absorbed at a rate of 1 ml in 2 to 4 minutes. After 46 hours, the hydrogenation was discontinued; 1320 ml of hydrogen had been absorbed. The acetic acid was driven off and the material distilled in vacuum. 1.2 g of 1,2-di-(p-methoxyphenyl)-3-methylcyclopentan-5-one (X) was obtained in the form of a light-yellow, extremely viscous liquid, b.p. 228-230° at 1.5 mm. This gave a crystalline oxime with m.p. 148.5° (from 50% alcohol).

4.980 mg substance. 0.188 ml N₂ (18°, 748 mm).
 5.590 mg substance. 0.203 ml N₂ (19°, 748 mm).
 Found %: N 4.36, 4.18.
 C₂₀H₂₃O₃N. Computed %: N 4.31.

In addition to the cyclopentanone (X) this experiment gave 3.4 g of a main fraction (boiling range 165-228° at 1.5 mm) which was not investigated further and was in all probability a mixture of the cyclopentanone (X) with the products of its further hydrogenation, in which the ketone group was reduced.

The demethylation of 1,2-di-(p-methoxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one. a) 1 g of the cyclopentenone (VII) was dissolved in a mixture of 3 ml of 48% hydrobromic acid and 3 ml of glacial acetic acid. The solution was heated at 120° for 45 minutes. The acids were then neutralized with 10% alkali, the alkaline solution was filtered, repeatedly extracted with ether, diluted with water to 20 ml, heated to boiling, and acidified with concentrated hydrochloric acid while undergoing vigorous stirring. The crystals which precipitated were filtered off, washed on the filter with 90% methanol, and recrystallized from 90% methanol. 700 mg of 1,2-di-(p-hydroxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VIII) was obtained in the form of light-yellow crystals which melted at 268°.

3.685 mg substance. 10.461 mg CO₂; 1.955 mg H₂O.
 3.990 mg substance. 11.339 mg CO₂; 2.115 mg H₂O.
 Found %: C 77.47, 77.55, H 5.80, 5.93.
 C₁₈H₁₆O₃. Computed %: C 77.1; H 5.71.
 0.0865 g substance. 13.70 ml methane (20°, 756 mm).
 0.0932 g substance. 15.95 ml methane (20°, 758 mm).
 Found %: OH 11.18, 11.92.
 C₁₈H₁₆O₃. Computed %: OH 12.14.

In the analysis (Tseizel) of the cyclopentenone (VIII), no methoxyl groups were detected.

The oxime of 1,2-di-(p-hydroxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one (VIII) melted at 223° (from 40% methanol).

4.080 mg substance. 0.162 ml N₂ (21°, 743 mm).

Found % N 4.577.

C₁₈H₁₇O₃N. Computed %: N 4.74.

b) A mixture of 5 ml of 48% hydrobromic acid, 5 ml of glacial acetic acid, and 2 g of the cyclopentenone (VII) was heated for 80 minutes at 110°. The acids were quickly driven off in vacuum (20 mm), the substance was dissolved in three percent caustic soda, the alkaline solution was filtered, heated to boiling, and acidified with concentrated hydrochloric acid. When the solution was cooled, the crystals which precipitated were removed, washed with 90% methanol, and boiled for 10 minutes with 5 ml of benzene. 0.9 g of the cyclopentenone (VIII) described above was obtained. This melted after recrystallization from 90% methanol at 268°. When the benzene solution was cooled, 0.2 g of white crystals precipitated out of it, these were the partially demethylated product, either cyclopentenone (XI) or (XII), with m.p. 172°.

3.159 mg substance. 9.052 mg CO₂, 1.850 mg H₂O.

4.319 mg substance. 12.364 mg CO₂, 2.520 mg H₂O.

Found %: C 78.02, 78.12; H 6.55, 6.53.

C₁₈H₁₈O₃. Computed %: C 77.55; H 6.17.

Found %: OCH₃ 10.78 (Tseizel).

C₁₈H₁₈O₃. Computed %: OCH₃ 10.91.

From the reaction flask of the Tseizel apparatus the cyclopentenone (VIII) was obtained, melting at 268°, and giving no lowering when mixed with the preceding sample, obtained from experiment (a).

c) A mixture of 10 ml of glacial acetic acid, 8 ml of hydrobromic acid which had been saturated at 15°, and 2 g of the cyclopentenone (VII) was heated for 4 hours at a temperature of 110°. The acids were quickly distilled off in vacuum, and the product was dissolved in 20 ml of 2% caustic soda, diluted with water to 100 ml, and the solution filtered. On the filter there was left 0.2 g of the original cyclopentenone (VII). The filtrate was acidified with concentrated hydrochloric acid, the precipitated crystals were filtered off, washed with 90% methanol, and with boiling benzene. After recrystallization from 90% methanol, 1.4 g of the cyclopentenone (VIII) was obtained, with b.p. 268°.

The reduction (Clemmensen) of 1,2-di-(p-hydroxyphenyl)-3-methyl- $\Delta^{1,2}$ -cyclopenten-5-one. 4 g of zinc filings were treated with a solution of 0.2 g of mercuric chloride in 4 ml of 3.5% hydrochloric acid for 10 minutes. After the amalgamating solution had been removed, there was poured over the zinc a mixture of 2 g of the cyclopentenone (VIII), 20 ml of glacial acetic acid, and 20 ml of concentrated hydrochloric acid. The reaction mixture was boiled for 4 hours, and 60 ml of water was then added to it, and the reaction product was carefully extracted with ether. The ether extract was washed four times with water, neutralized with sodium bicarbonate, and dried over magnesium sulfate. After the ether had been driven off, the substance was distilled in vacuum. 1.4 g of 1,2-di-(p-hydroxyphenyl)-3-methylcyclopentane (IX) was obtained in the form of an extremely viscous light-yellow non-crystalline mass. B.p. 215-220° at 0.06 mm.

4.980 mg substance. 14.705 mg CO₂, 3.525 mg H₂O.

5.160 mg substance. 15.240 mg CO₂, 3.640 mg H₂O.

Found %: C 80.58, 80.60; H 7.92, 7.89.

C₁₈H₂₀O₂. Computed %: C 80.51; H 7.46.

The synthesis of ethyl-p-methoxyphenyl ketone. To 80 g of aluminum chloride which was placed under a layer of carbon disulfide (200 ml) there was added in a period of a half hour, at a temperature of 25 to 30°, 80 g of propionyl chloride. Then, at -5°, 60 g of anisole was added. The reaction mixture was stirred for 1 hour at room temperature. The carbon disulfide layer was removed, washed with water and sodium bicarbonate, dried with potash, and the carbon disulfide driven off. The product was then distilled in vacuum. 65 g of ethyl-p-methoxyphenyl ketone was obtained. B.p. 107° at 2 mm; n_D^{18} 1.5477.

The synthesis of ethyl-p-methoxyphenyl vinyllethynyl carbinol and of 5-p-methoxyphenyl-1,5-heptadien-3-ine. To an ether solution of vinylacetylenyl magnesium bromide, prepared from 13 g of magnesium, 64 g of ethyl bromide, 70 g of vinylacetylene, and 300 ml of ether, 62 g of ethyl-p-methoxyphenyl ketone was added at 35°. The reaction mixture was heated for 2 hours until the ether boiled vigorously. It was then cooled and decomposed with 30 ml of water. The ether layer was poured off and the precipitate was washed three times with ether. The united ether extracts were dried with magnesium sulfate, and the ether then driven off in vacuum. About 70 g of crude ethyl-p-methoxyphenyl-vinylethynyl carbinol (XVI) was obtained in the form of an extremely viscous dark-yellow liquid. Upon heating in vacuum to 60°, this carbinol split off water and was converted into 5-p-methoxyphenyl-1,5-heptadien-3-ine (XVII), which was distilled in vacuum. 60 g of 5-p-methoxyphenyl-1,5-heptadien-3-ine (XVII) was obtained in the form of a light yellow liquid with a pleasant odor.

B.p. 132° at 1.5 mm; n_D^{20} 1.6003; d_4^{20} 1.019, MR found 66.80, computed 61.62.

11.03 mg substance: 33.70 mg CO₂, 7.59 mg H₂O.

13.59 mg substance: 41.55 mg CO₂, 9.09 mg H₂O.

Found %: C 83.33, 83.46; H 7.70, 7.48.

C₁₄H₁₄O. Computed %: C 84.8; H 7.07.

The hydrogenation of 5-p-methoxyphenyl-1,5-heptadien-3-ine. 3 g of the diene (XVII) was hydrogenated with Pt catalyst in a solution of 20 ml of methanol. 1370 ml of hydrogen (4 mol.) was absorbed. Most of the hydrogen was absorbed in 2 hours. The methanol was driven off and the substance fractionated in vacuum. 1.5 g of 5-p-methoxyphenylheptane (XXI) was obtained.

B.p. 92.7-93° at 1.5 mm, n_D^{20} 1.4967, d_4^{20} 0.922, MR found 64.87; computed 65.2.

7.46 mg substance: 21.86 mg CO₂; 7.10 mg H₂O.

Found %: C 79.97; H 10.65.

C₁₃H₂₂O. Computed %: C 80.30; H 11.33.

The hydration of 5-p-methoxyphenyl-1,5-heptadien-3-ine. 8 g of the diene (XVII) and 1 g of mercuric sulfate were added to a solution of 1 g of concentrated sulfuric acid in 100 ml of 95% methanol. The solution was vigorously stirred for 12 hours at 65°. Both 4 and 8 hours after the beginning of the reaction, 0.5 g portions of mercuric sulfate were added to the reaction mixture. The methanol was driven off in vacuum (100 mm) and the substance was extracted with ether, washed with sodium bicarbonate, dried with calcium chloride, and after the ether had been driven off, distilled in vacuum. 6.5 g of a mixture of 5-p-methoxyphenyl-1,5-heptadien-4-one (XVIII) and 1-p-methoxyphenyl-2,3-dimethyl- $\Delta^{1,2}$ -cyclopenten-5-one (XIX) was obtained, boiling within the limits 140 to 160° at 1.5 mm, n_D^{20} 1.5595. The mixture was heated for 10 minutes with 0.1% p-toluene-sulfonic acid at 155°, and then quickly distilled in a vacuum of 1.5 mm. The vacuum distillation gave 5 g of 1-p-methoxyphenyl-2,3-dimethyl- $\Delta^{1,2}$ -cyclopenten-5-one (XIX) in the form of a light yellow extremely viscous liquid with a pleasant honey odor. B.p. 150° at 1.5 mm; n_D^{20} 1.5775.

13.96 mg substance. 38.90 mg CO₂. 8.74 mg H₂O.
 12.13 mg substance. 34.48 mg CO₂. 7.90 mg H₂O.
 Found % C 77.54, 77.58; H 7.13, 7.27.
 C₁₅H₁₄O₂. Computed % C 77.68; H 7.41.

The semicarbazone of the cyclopentenone (XIX) melted at 204.5° (from alcohol).

4.253 mg substance. 0.578 ml N₂ (21°, 758 mm).
 5.160 mg substance. 0.691 ml N₂ (22°, 744 mm).
 Found % N 15.52, 15.17.
 C₁₅H₁₀O₂N₂. Computed % N 15.36.

The demethylation of 1-p-methoxyphenyl-2,3-dimethyl-Δ^{1,2}-cyclopenten-5-one. 0.5 g of the cyclopentenone (XIX) was heated for 2 hours at 120° with a mixture of 6 ml of glacial acetic acid and 3 ml of hydrobromic acid which had been saturated at 25°. The acids were driven off in vacuum (30 mm) and the substance was dissolved in 5 ml of 10% alkali. In order to remove the unreacted methoxyketone from the residues, the alkali solution was carefully extracted with ether, and then acidified with concentrated hydrochloric acid. The substance was extracted with ether, dried over calcium chloride, and after removal of the ether, distilled in vacuum. 0.4 g of a vitreous substance with b.p. 175-177° at 0.04 mm was obtained. After it was rubbed with a glass rod, it crystallized. After recrystallization from benzene, 0.37 g of 1-p-hydroxyphenyl-2,3-dimethyl-Δ^{1,2}-cyclopenten-5-one was obtained (XX) in the form of colorless crystals which melted at 134°.

13.69 mg substance. 38.90 mg CO₂. 8.74 mg H₂O.
 12.13 mg substance. 34.48 mg CO₂. 7.90 mg H₂O.
 Found % C 77.54, 77.58; H 7.13, 7.27.
 C₁₅H₁₄O₂. Computed % C 77.22; H 6.92.

The authors express their thanks to Prof. V.I. Maksimov and to their scientific colleague I.N. Lektorsky for carrying out the experiments on estrogenic activity described in this article with the compounds (VII, VIII, and IX).

SUMMARY

The action of vinylacetylenyl magnesium bromide on desoxyanisoin (I) gave a more than 90% yield of p-methoxyphenyl-p-methoxybenzylvinylethynyl carbinol (II). The dehydration of this latter compound gave 5,6-di-(p-methoxyphenyl)-1,5-hexadien-3-ine (III) in good yield. Upon heating the diene (III) in aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate, the dienone (VI) was formed, and this during the very process of this reaction was partially cyclized to give 1,2-di-(p-methoxyphenyl)-3-methyl-Δ^{1,2}-cyclopenten-5-one (VII). Thus, the diene (III) can be almost completely converted into the cyclopentenone (VII) by the method of hydration and cyclization, and the latter, by means of hydrobromic acid in a solution of glacial acetic acid can be smoothly demethylated to give 1,2-di-(p-hydroxyphenyl)-3-methyl-Δ^{1,2}-cyclopenten-5-one (VIII). Careful demethylation of the cyclopentenone (VII) also gave a product of incomplete demethylation, with the structure XI or XII.

The cyclopentenone (VIII) was reduced by the Clemmensen method to 1-methyl-2,3-di-(p-hydroxyphenyl)-cyclopentanone (IX). The hydrogenation of the diene (III) and of the cyclopentenone (VII) is described, as well as the process of demethylation of 5,6-di-p-methoxyphenyl-1,5-hexadien-3-ine (III).

The compounds VII, VIII, and IX did not show estrogenic activity when tried on an infarile mice in doses up to 100 mg.

The action of vinylacetylenyl magnesium bromide on p-methoxyphenylethyl ketone also resulted in the synthesis of 1-p-methoxybenzylvinylethynyl carbinol.

(XVI) which, upon heating, spontaneously lost water to give 5-p-methoxyphenyl-1,5-heptadien-3-ine (XVII). The dienine (XVII), upon heating in aqueous solutions of methanol was hydrated fairly slowly, but in good yield, to give 5-p-methoxyphenyl-1,5-heptadien-4-one (XVIII), which under the conditions of hydration was partially cyclized into 1-(p-methoxyphenyl)-2,3-dimethyl- $\Delta^{1,2}$ -cyclopenten-5-one (XIX).

The dienone (XVIII) was easily cyclized into the cyclopentenone (XIX) also by a short period of heating with 0.1% p-toluenesulfonic acid. The cyclopentenone (XIX) was demethylated by a mixture of glacial and hydrobromic acids to give 1-(p-hydroxyphenyl)-2,3-dimethyl- $\Delta^{1,2}$ -cyclopenten-5-one (XX).

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ACETYLENE DERIVATIVES

115. THE MECHANISM OF HYDRATION AND CYCLIZATION OF DIENINES

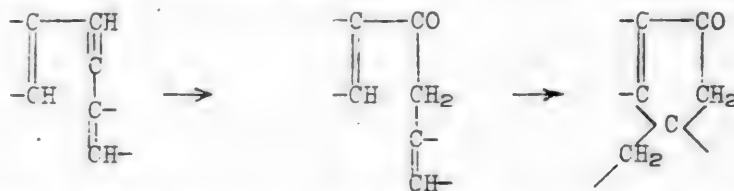
XXIV The Hydration of 5-Phenyl-6-Methyl-1,5-Heptadien-3-ine
to Give 5-Phenyl-6-Methyl-1,5-Pentadien-4-one and its Cyclization
to Give 1-Phenyl-2,2,3-Trimethyl- $\Delta^{3,4}$ -Cyclopenten-5-one.

A New Type of Cyclization of Substituted Vinyl Allyl Ketones,
which do not have Free Hydrogens in the Vinyl Radical

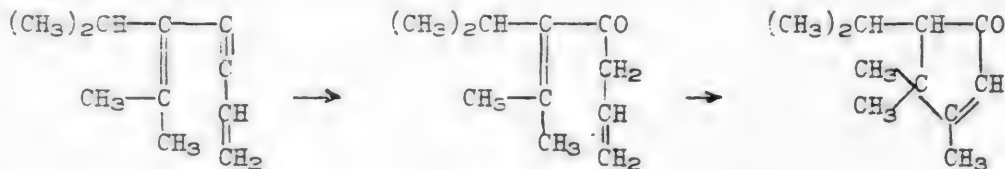
I. N. Nazarov and I. L. Kotlyarevsky

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In our laboratory, in the course of the past six years, we have shown by numerous examples that the substituted vinyl allyl ketones obtained by the hydration of dienines are cyclized with extreme ease, and in the majority of cases almost quantitatively, under the influence of acids (phosphoric and others) to give the corresponding cyclopentenones [1].



As can be seen from this equation, all these cyclizations usually take place because of the free hydrogen on the end of the vinyl group of the dienone. However, it has been found of late in our laboratory that cyclization to give cyclopentenones can also be carried out with those dienones (substituted vinyl allyl ketones) which do not have a free hydrogen on the vinyl radical. This was illustrated by the following example [2]:

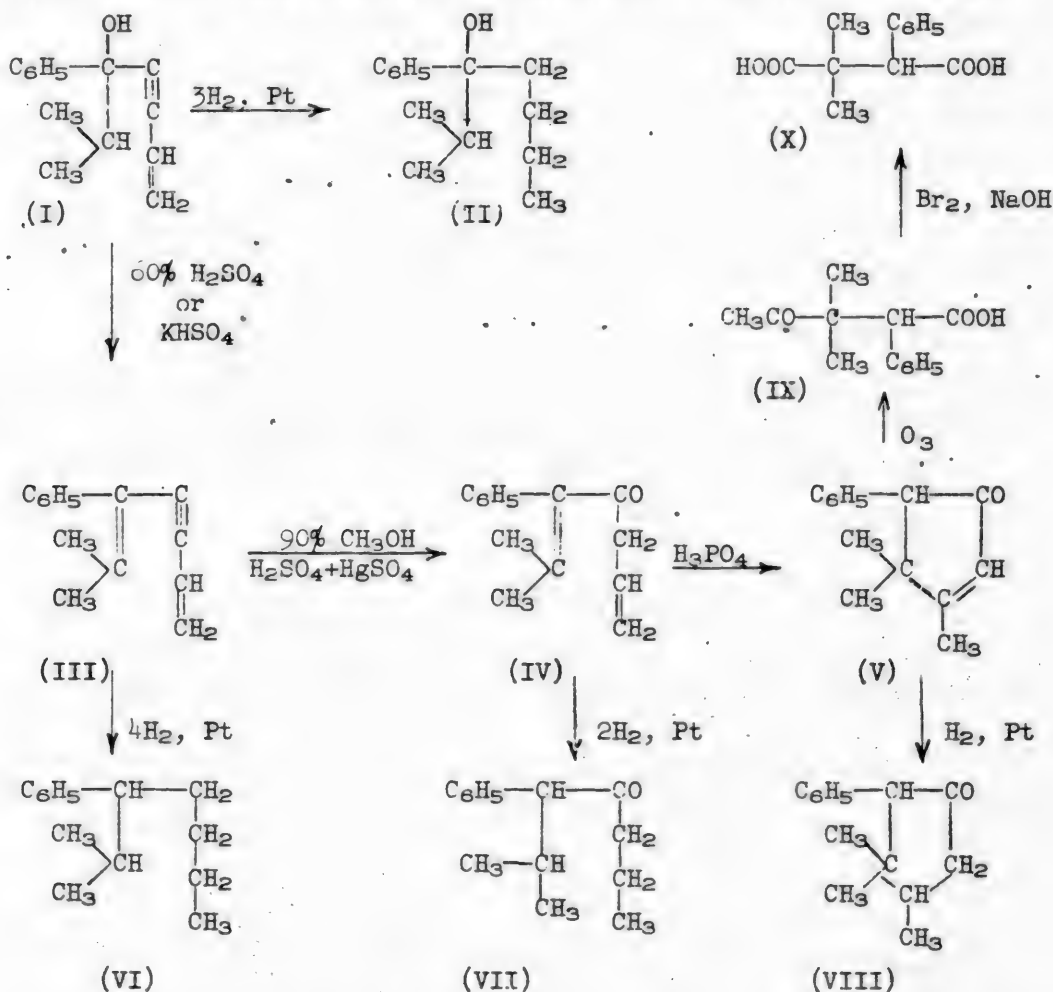


The cyclization of 5-isopropyl-6-methyl-1,5-heptadien-4-one to give 1-isopropyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one takes place quantitatively under the influence of phosphoric acid even at room temperature.

This cyclization is of especial interest for an understanding of the mechanism of these processes. It shows that in order to carry out the cyclization of vinyl allyl ketones into cyclopentenones, the presence of a free hydrogen in the vinyl group is not obligatory, and that these cyclization can also take place

easily because of the free hydrogens of the allyl radical. It became very desirable and necessary to investigate these interesting cyclizations in other examples as well. As the starting material for these investigations we used isopropylphenylvinylethynyl carbinol (I), obtained in a yield of about 90% by the action of vinylacetylenyl magnesium bromide on isopropylphenyl ketone. Upon hydrogenation of the carbinol (I) in the presence of Pt catalyst, three molecules of hydrogen were absorbed, and isopropylbutylphenyl carbinol (II) was formed.

The dehydration of the carbinol (I) by means of 60% sulfuric acid or potassium bisulfate gave 5-phenyl-6-methyl-1,5-heptadien-3-ine (III), which upon heating in aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate was smoothly hydrated to 5-phenyl-6-methyl-1,5-heptadien-4-one (IV). Upon hydrogenating the dienone (IV) with Pt catalyst, the required theoretical amount of four molecules of hydrogen were absorbed, and 5-phenyl-6-methylheptane (VI) was formed; but during a similar hydrogenation of the dienone (IV) two molecules of hydrogen were absorbed, and 5-phenyl-6-methylheptan-4-one (VII) was formed.



Under the influence of acids (phosphoric, sulfuric, hydrochloric, p-toluenesulfonic) the dienone (IV) was completely cyclized with the formation of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V). This cyclization under the influence of phosphoric acid, as also in the case of 5-isopropyl-6-methyl-1,5-heptadien-4-one, took place easily even at room temperature (with decomposition).

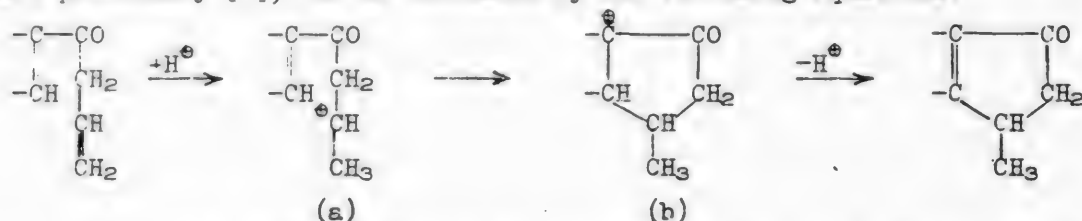
The cyclopentenone (V), upon hydrogenation with Pt catalyst, absorbed one

molecule of hydrogen and was converted into 1-phenyl-2,2,3-trimethylcyclopentan-5-one (VIII).

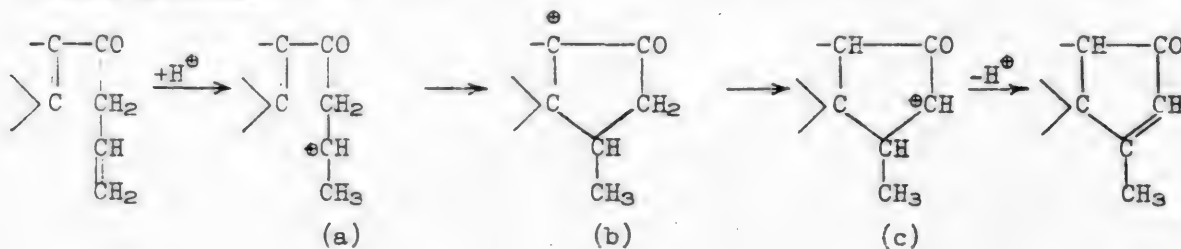
The structure of the cyclopentenone (V) was decisively demonstrated by means of ozonization, during which a high yield of formic acid and of α -phenyl- β,β -dimethyllevulinic acid (IX) was obtained. The latter was then oxidized with alkaline bromine to give the well-known α,α -dimethyl- α' -phenylsuccinic acid (X) [3].

The carbinol (I) and the dienine (III), as distinguished from the aliphatic and alicyclic vinyl ethinyl carbinols and the dienines which correspond to them, are incapable of being directly converted into the cyclopentenone (V) under the influence of phosphoric acid. This is to be explained by the inability of the aromatic dienines to become hydrated to the corresponding dienones under these conditions. The hydration of the aromatic dienines can take place smoothly only in the presence of a mercury catalyst.

All the cyclization reactions of the substituted vinyl allyl ketones to give cyclopentenones take place only in acid medium, and therefore, the hydrogen ion must be the initiator of these cyclizations. Therefore the most probable mechanism of these reactions, as has already been developed by one of us in detail previously [4], can be indicated by the following equations:



In case the dienone does not have a free hydrogen in the vinyl radical, and the cyclized ion (b) which is formed cannot therefore be stabilized, the isomerization of the cyclic ion (b) takes place, with the shift of a hydrogen and the formation of a new cyclic ion (c), which is then also stabilized by the release of a proton to give a cyclopentenone, but with the double bond in a different position:



EXPERIMENTAL

The synthesis of isopropylphenylketone. The acid chloride of isobutyric acid was obtained in 85% yield by the reaction of silicon tetrachloride (2 mol.) with isobutyric acid (1 mol.) at 50° for a period of an hour.

To a mixture of 150 g of ground aluminum chloride and 200 ml of dry benzene there was added over a period of an hour, with vigorous stirring, 95 g of the acid chloride of isobutyric acid. The mixture was then poured over ice, the benzene layer removed, the aqueous layer extracted with benzene, and the united benzene extract washed with sodium bicarbonate, dried over magnesium sulfate, and the benzene driven off. The product was distilled in vacuum. 103 g of isopropylphenyl

ketone was obtained with b.p. 75.6° at 2 mm; n_D^{20} 1.5710 [s].

The synthesis of isopropylphenylvinylethynyl carbinol. To an ether solution of vinylacetylenyl magnesium bromide prepared from 31 g of magnesium, 145 g of ethyl bromide, 400 ml of absolute ether, and 100 g of vinylacetylene, there was added at a temperature of 35° in a period of 30 minutes 102 g of isopropylphenyl ketone. The reaction mixture was then heated for 10 hours until there was vigorous boiling of the ether, and allowed to stand for 12 hours at room temperature. After 0.2 g of hydroquinone had been added, the product was slowly hydrolyzed at 0° with water (30 ml) and then, in order to dissolve the precipitate, there was added, drop by drop, 260 ml of 15% hydrochloric acid. The ether extract was washed with sodium bicarbonate dried over magnesium sulfate, and the ether driven off. The product was then fractionated in vacuum. 116 g of isopropylphenylvinylethynyl carbinol (I) was obtained in the form of a viscous, colorless liquid:

B.p. 108° at 2 mm; n_D^{19} 1.5477; d_4^{20} 1.018; MR found 63.52; computed 62.27

6.475 mg substance. 19.856 mg CO₂, 4.805 mg H₂O.

5.550 mg substance. 17.009 mg CO₂, 3.995 mg H₂O.

Found %. C 83.69, 83.74; H 8.30, 8.05.

C₁₄H₁₆O. Computed %. C 83.92; H 7.99.

The hydrogenation of isopropylphenylvinylethynyl carbinol. 2 g of the carbinol (I) was hydrogenated with Pt catalyst in a solution of 20 ml of alcohol. 670 ml of hydrogen (3 mol.) were absorbed. The alcohol was driven off, and the substance fractionated in vacuum. 1.8 g of isopropylphenylvinylethynyl carbinol (II) was obtained:

B.p. 107-108° at 3 mm; n_D^{19} 1.5102; d_4^{20} 0.9562; MR found 64.38; computed 64.74.

3.637 mg substance. 10.821 mg CO₂; 3.401 mg H₂O.

Found %. C 81.20; H 10.46.

C₁₄H₂₂O Computed %. C 81.52; H 10.69.

The dehydration of isopropylphenylvinylethynyl carbinol. a) 40 g of the carbinol (I) and 70 ml of 60% sulfuric acid were vigorously stirred for 30 minutes at 70°. The mixture was diluted with water (100 ml), extracted with ether, the ether extract washed with a solution of sodium bicarbonate, dried with magnesium sulfate, and the ether driven off. The substance was fractionated in vacuum. 17 g of 5-phenyl-6-methyl-1,5-heptadien-3-ine (III) was obtained in the form of a light-yellow liquid with a flowery odor.

B.p. 94-95° at 1.5 mm; n_D^{17} 1.5772 d_4^{20} 0.956; MR found 63.15; computed 60.28.

5.715 mg substance. 18.607 mg CO₂, 4.019 mg H₂O.

6.215 mg substance. 20.236 mg CO₂, 4.247 mg H₂O.

Found %. C 88.85, 88.86; H 7.86, 7.64.

C₁₄H₁₄. Computed %. C 92.22, H 7.78

Upon standing, the dienine (III) darkened and was oxidized. This also explains the lowering of the carbon content in its analysis.

b) 15 g of the carbinol (I) and 5 g of powdered potassium bisulfate were heated at 160° for 7 minutes in a vacuum of 20 mm. The product was then quickly distilled in vacuum (3-4 mm). After the water had been removed, this operation was repeated twice more. There was finally obtained 7.5 g of the 5-phenyl-6-methyl-1,5-heptadien-3-ine (III) described above.

B.p. 94-95° at 1.5 mm; n_D^{18} 1.5770.

The hydrogenation of 5-phenyl-6-methyl-1,5-heptadien-3-ine. 1.7 g of the dienine (III) was hydrogenated in a solution of glacial acetic acid with Pt

catalyst. 820 ml of hydrogen (4 mol.) were absorbed. The acetic acid was driven off, the substance diluted with ether, washed with a solution of sodium bicarbonate, dried with magnesium sulfate, and the ether driven off. The substance was then distilled in vacuum. 1.2 g of 5-phenyl-6-methylheptane (VI) was obtained.

B.p. 71-72° at 2 mm; n_D^{19} 1.4980; d_4^{20} 0.8875; MR found 62.8; computed 63.2.

5.360 mg substance. 17.356 mg CO₂; 5.260 mg H₂O.

5.120 mg substance. 16.590 mg CO₂; 5.040 mg H₂O.

Found %: C 88.37, 88.43; H 10.98, 11.01.

C₁₄H₂₂ Computed %: C 88.32, H 11.68.

The hydration of 5-phenyl-6-methyl-1,5-heptadien-3-ine. 36 g of the diene and 6 g of mercuric sulfate were added to a solution of 10 ml of concentrated sulfuric acid in 450 ml of 95% methanol. The reaction mixture was stirred vigorously for 1.5 hours at 65°, and 6 g more of mercuric sulfate then added, and the stirring was continued at the same temperature for an additional 1.5 hours. The methanol was driven off in vacuum (100 mm), and the substance was dissolved in ether, washed with a solution of sodium bicarbonate, dried with magnesium sulfate, and the ether driven off. The substance was then distilled in vacuum. 34 g of a mixture of 5-phenyl-6-methyl-1,5-heptadien-4-one (IV) and the methoxy ketone corresponding to it, with boiling range from 110 to 130° at 2 mm, was obtained. In order to split the methanol off from the methoxyketone, the mixture obtained was distilled in the presence of 20 mg of p-toluenesulfonic acid in a vacuum of 3 mm. The substance thus obtained was fractionated in vacuum;

The 1st fraction had b.p. 110-112° at 2 mm, 12 g; 2nd fraction, b.p. 112-129° at 2 mm, 6 g, 3rd fraction b.p. 129-130° at 2 mm, 7.5 g.

The first fraction consisted of 5-phenyl-6-methyl-1,5-heptadien-4-one (IV), and was a light yellow oil with a pleasant odor.

B.p. 110-112° at 2 mm; n_D^{20} 1.5480; d_4^{20} 1.002; MR found 63.3; computed 62.28.

5.270 mg substance. 16.172 mg CO₂; 3.795 mg H₂O.

4.760 mg substance; 14.620 mg CO₂; 3.415 mg H₂O.

Found %: C 83.74, 83.82; H 8.06, 8.03.

C₁₄H₁₆O. Computed %: C 83.92; H 7.99.

An attempt to obtain the semicarbazone of this dienone did not lead to positive results.

The third fraction was 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V), and was a colorless crystalline substance, which crystallized slowly after distillation:

B.p. 129-130° at 2 mm; m.p. 40° (from 80% alcohol). n_D^{20} 1.5520; d_4^{20} 1.044; MR found 61.15; computed 60.55.

4.487 mg substance. 13.718 mg CO₂; 3.230 mg H₂O.

3.410 mg substance. 10.457 mg CO₂; 2.485 mg H₂O.

Found %: C 83.43, 83.69; H 8.05, 8.15.

C₁₄H₁₆O. Computed %: C 83.92; H 7.99.

The semicarbazone of the cyclopentenone (V) melted with decomposition at 222.5° (from alcohol).

4.440 mg substance. 0.631 ml N₂ (21°, 753 mm).

3.090 mg substance. 0.446 ml N₂ (22°, 749 mm).

Found %: N 16.50, 16.46.

C₁₅H₁₈CN₃. Computed %: N 16.35.

The second fraction was a mixture of the dienone (IV) and the cyclopentenone (V). This was treated for the purpose of isolating the dienone with 3 ml

of phosphoric acid (sp. gr. 1.82). This resulted in the temperature of the mixture rising to 60°. After 15 minutes of heating at 70°, the product was diluted with water, the substance extracted with ether, washed with a solution of sodium bicarbonate, dried over magnesium sulfate, and the ether driven off. The substance was then distilled in vacuum to give 5 g of the cyclopentenone (V) described above:

B.p. 129-130° at 2 mm; n_D^{20} 1.5520; m.p. 46° (from 80% alcohol).

The hydrogenation of 5-phenyl-6-methyl-1,5-heptadien-4-one. 2 g of the dienone (IV) were hydrogenated with Pt catalyst in a solution of 20 ml of glacial acetic acid. 450 ml of hydrogen (2 mol.) were absorbed, the first molecule of hydrogen (220 ml) being absorbed quickly and the second molecule of hydrogen being absorbed very slowly. The acid was driven off and the ketone distilled in vacuum. 1.6 g of 5-phenyl-6-methylheptan-4-one (VII) was obtained

B.p. 104-105° at 2 mm; n_D^{19} 1.5175; d_4^{20} 0.971; MR found 63.4. Computed 62.54. The semicarbazone of this ketone melted at 192° (from alcohol).

3.350 mg substance: 0.405 ml N_2 (22°, 756 mm).

Found %: N 15.98.

$C_{15}H_{23}ON_3$. Computed %: N 16.04.

The cyclization of 5-phenyl-6-methyl-1,5-heptadien-4-one. a) 12 g of the dienone (IV) (b.p. 110-112° at 2 mm, n_D^{20} 1.5480) were poured with continual stirring into 15 g of concentrated phosphoric acid (sp. gr. 1.82). The mixture evolved enough heat to reach a temperature of 85°, and quickly became completely uniform. The product was kept for 40 minutes at 70°, diluted with water, extracted with ether, washed with a solution of sodium bicarbonate, dried with magnesium sulfate, and the ether driven off. It was then distilled in vacuum. 10 g of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V) were obtained, with b.p. 129-130° at 2 mm; n_D^{20} 1.5520; m.p. 46° (from 80% alcohol). The semicarbazone of this cyclopentenone melted at 221.5° and did not cause lowering of the melting point when mixed with the sample described above.

b) 3 g of the dienone (IV) (b.p. 110-112° at 2 mm, n_D^{20} 1.5480) were heated in a vacuum of 2 mm with 20 mg of p-toluenesulfonic acid for 40 minutes at 160°. A vacuum distillation gave 2.2 g of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one, b.p. 129-130° at 2 mm, m.p. 46°, identical with the sample described above.

Thus, the cyclization of 5-phenyl-6-methyl-4,5-heptadien-4-one took place during the treatment both with phosphoric acid and with p-toluenesulfonic acid.

The hydrogenation of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one. 4 g of the cyclopentenone (V) (b.p. 129-130° at 2 mm) were hydrogenated with Pt catalyst in a solution of 20 ml of methanol. The hydrogenation took place rapidly and was complete after 4 hours, most of the hydrogen being absorbed during the first half hour. A total of 440 ml of hydrogen (1 mol) was absorbed. The methanol was driven off and the substance distilled in vacuum. 3.8 g of 1-phenyl-2,2,3-trimethylcyclopentan-5-one (VIII) were obtained:

B.p. 119-120° at 2 mm, n_D^{20} 1.5345, d_4^{20} 1.025; MR found 61.18. computed 61.02.

Semicarbazone: 4.010 mg substance. 0.565 ml N_2 (19°, 750 mm).

4.120 mg substance: 0.589 ml N_2 (21°, 750 mm).

Found %: N 16.30, 16.31.

$C_{15}H_{21}CN_3$. Computed %: N 16.23.

The semicarbazone of this ketone melted without decomposition at 223° (from alcohol).

A mixed test with the semicarbazone of the cyclopentanone (V) melted at 217°.

Upon hydrogenation in glacial acetic acid, 1 molecule of hydrogen was also absorbed and the same substance was obtained as by hydrogenation in methanol.

The ozonation of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one. 7 g of the cyclopentenone (V) in a solution of 30 ml of dry chloroform was ozonized over a period of 10 hours with oxygen containing 6% of ozone, with a velocity of 4 liters per hour. The chloroform was driven off in vacuum, and the ozonides decomposed by stirring for 4 hours with 50 ml of water at 90°. The mixture was neutralized with sodium bicarbonate, and treated with ether to extract neutral products, of which, however, almost none were present. One-fortieth of the solution of the salts was utilized for a determination of formic acid by the calomel method. This gave 0.145 g of calomel, which corresponded to a total formic acid content in the solution of 0.57 g, or 36% of the theoretical.

The solution of the salts of organic acids was then acidified with concentrated hydrochloric acid, and the voluminous precipitate which formed was filtered off, and recrystallized twice from hot water. 6 g of α -phenyl- β,β -dimethyllevulinic acid (IX) was obtained, with m.p. 140°. The filtrate was neutralized with bicarbonate, evaporated to dryness, the salts treated with concentrated hydrochloric acid, and the acids extracted with ether. Thus, an additional 0.3 g of α -phenyl- β,β -dimethyllevulinic acid was obtained, which melted at 140° (from water). The total yield of this acid was 6.3 g.

The semicarbazone of the α -phenyl- β,β -dimethyllevulinic acid was obtained, with m.p. 197° (from alcohol).

4.420 mg substance. 0.580 ml N_2 (22°, 751 mm).

3.060 mg substance. 0.407 ml N_2 (20°, 747 mm).

Found %: N 15.01, 15.11.

$C_{14}H_{18}O_3$. Computed %: N 15.16.

0.0762 mg substance. 17.93 g dioxane. Δt 0.094°.

Found. M 214.

$C_{14}H_{18}O_3$. Computed. M 220.

0.2414 g substance. 10.92 ml 0.1 N NaOH.

0.3202 g substance. 14.62 ml 0.1 N NaOH.

Found: M 221, 219.5.

Computed. M 220.

The oxidation of α -phenyl- β,β -dimethyllevulinic acid. 0.55 g of α -phenyl- β,β -dimethyllevulinic acid was dissolved in 15 ml of 10% caustic soda, and to the solution there was added, drop by drop, with cooling by ice water, 1.7 g of bromine. A voluminous white precipitate came out, and in the course of 3 hours of stirring this gradually went into solution, emitting a strong odor of bromoform which separated out on the bottom of the flask in the form of heavy drops. The solution was acidified with 18% hydrochloric acid (7.5 ml), and a precipitate of 0.4 g of α,α -dimethyl- α -phenylsuccinic acid (X) formed. After recrystallization from water, this melted at 172°.

3.854 mg substance. 9.156 mg CO_2 , 2.233 mg H_2O .

3.731 mg substance. 8.867 mg CO_2 , 2.275 mg H_2O .

Found %: C 64.98, 64.85, H 6.50, 6.28.

$C_{12}H_{14}O_4$. Computed %: C 64.80, H 6.31.

0.0320 g substance. 2.87 ml 0.1 N NaOH.

Found: M 227.3.

$C_{12}H_{14}O_4$. Computed. M 222.

The cyclization-hydration of 1-phenyl-6-methyl-1,5-heptadien-3-ine. 2 g of the diene (III) and 3 ml of phosphoric acid (sp. gr. 1.8) were stirred for 3 hours at a temperature of 70 to 80°. The product was diluted with water,

extracted with ether, washed with sodium bicarbonate, and dried with calcium chloride. After the ether had been driven off, the substance was distilled in vacuum. A total of 0.2 g of liquid came over, boiling within the limits 90 to 130° at 2 mm. 1.6 g of tar remained in the flask. From the distilled liquid it was possible to obtain a semicarbazone, which, after recrystallization from alcohol, melted at 221°, and gave no depression of the melting point with the semicarbazone, which had been described above, of 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V).

SUMMARY

The action of vinylacetylenyl magnesium bromide on phenylisopropyl ketone gave an 85% yield of phenylisopropylvinylethynyl carbinol (I). Upon dehydration with 60% sulfuric acid or potassium bisulfate, this gave 5-phenyl-6-methyl-1,5-heptadien-3-ine (III). This dienine, upon heating in aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate, was hydrated in good yield to give 5-phenyl-6-methyl-1,5-heptadien-4-one (IV), and the latter, upon distillation with p-toluenesulfonic acid or upon treatment with phosphoric acid was completely cyclized into 1-phenyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V). Thus it has been shown that in order to cyclize 1,5-dien-4-ones (substituted vinyl allyl ketones) to cyclopentenones, the presence of a free hydrogen atom on the end carbon of the vinyl radical is not indispensable, and that this cyclization can also take place by means of the hydrogens of the allyl group.

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DERIVATIVES OF ACETYLENE

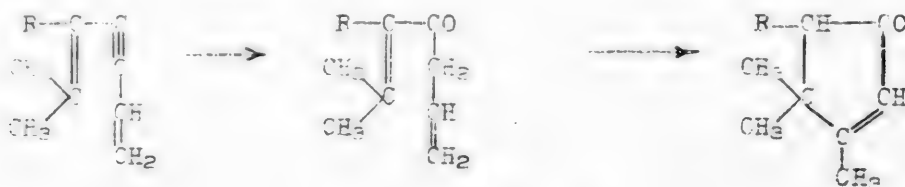
116 THE MECHANISM OF THE HYDRATION AND CYCLIZATION OF DIENINES.

XXV The Hydration of β -Tert-Butyl-6-Methyl-1,5-Heptadien-3-ine and the Cyclization of the β -Tert-Butyl-6-Methyl-1,5-Heptadien-4-one thus Formed to Give 1-Tert-Butyl-2,2,3-Trimethyl-3,4,5-Cyclopenten-5-one.

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In our laboratory we have recently found a new type of cyclization of substituted vinyl allyl ketones which do not have free hydrogen atoms in the vinyl radical. These cyclizations take place according to the following general equations. [1,2]



$\text{R} = \text{iso-C}_2\text{H}_5\text{- and C}_6\text{H}_5$

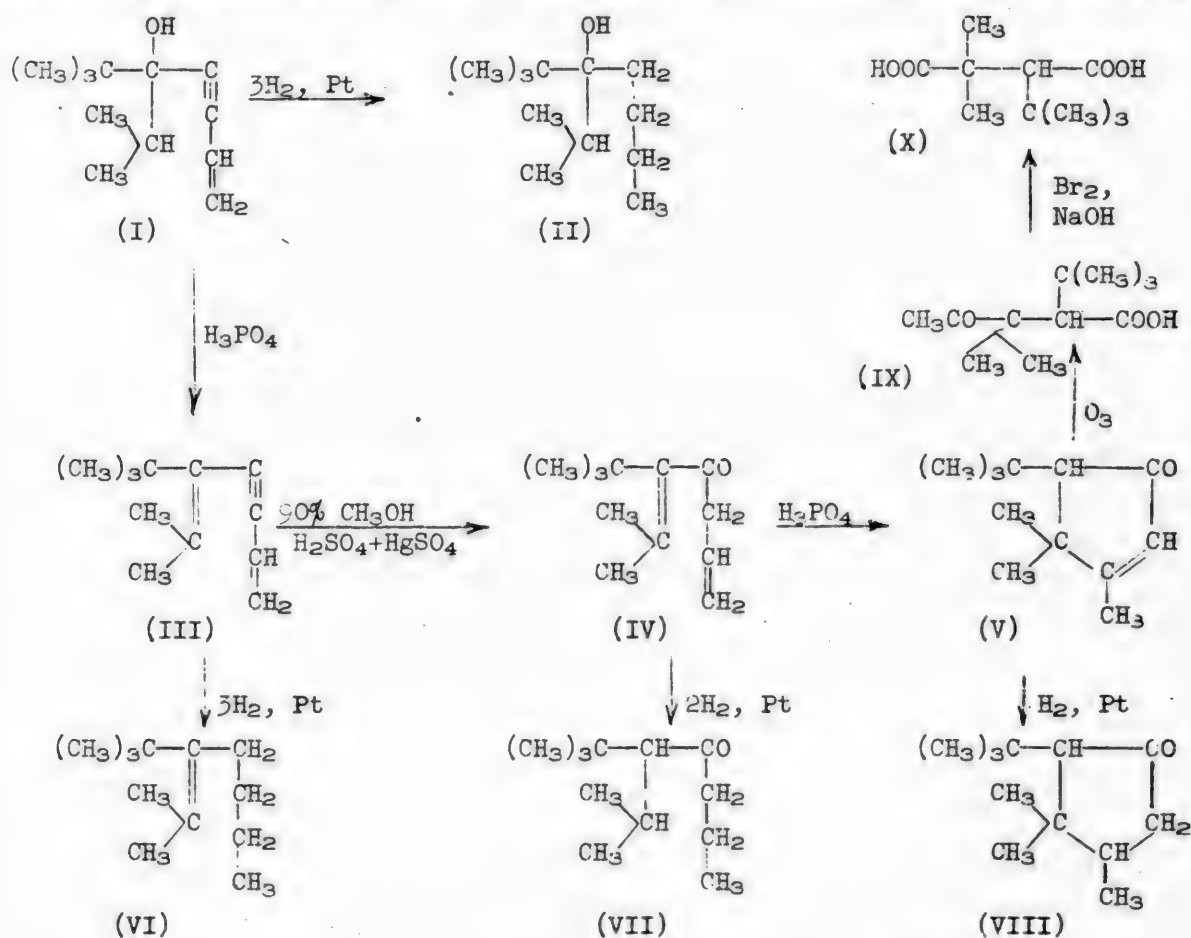
In these new examples, the cyclization of vinyl allyl ketones takes place not because of a hydrogen of the vinyl radical, as had been shown in numerous previous examples [3,4], but because of the hydrogens of the allyl group, and leads to the formation of cyclopentenones with the double bond in other positions in the ring ($\Delta^{3,4}$ -cyclopenten-5-ones instead of $\Delta^{1,2}$ -cyclopenten-5-ones).

The mechanism of these interesting and very easily effected cyclizations was explained on the basis of a single group of equations, which were in turn based on the idea of the formation of positively charged cyclic ions.

In our present article we have continued our study of these cyclizations, and have chosen as our starting material isopropyl-tert. butylvinylallyl carbinol (I), which was obtained in a yield of about 90% by the action of vinylacetyl-ethyl magnesium bromide on pentamethylacetone. The carbinol (I), upon hydrogenation with Pt catalyst, absorbs three molecules of hydrogen and gives isopropyl-n-butyl-tert. butyl carbinol (II). When the carbinol (I) was dehydrated by means of phosphoric acid (sp. gr. 1.7) an approximately 70% yield of β -tert. butyl-6-methyl-1,5-heptadien-3-ine (III) was obtained, and this, upon hydrogenation with Pt catalyst in a solution of glacial acetic acid, absorbed only three molecules of hydrogen (instead of the four required by theory), and gave an olefin which was in all probability β -tert. butyl-6-methyl-4-heptene (IV). Similar olefin hindrance has been frequently observed previously during the catalytic hydrogenation of a branched double bond, both by other authors [4] and in our own laboratory.

When the dienine (III) was hydrated in aqueous solutions of methanol, in the presence of sulfuric acid and mercuric sulfate, 5-tert. butyl-6-methyl-1,5-heptadien-4-one (IV) was obtained, and this, under the influence of phosphoric acid, was easily cyclized to 1-tert.-butyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V).

As a result of the presence of a heavy branched radical (tert. butyl) alongside the triple bond, the dienine (III) was hydrated at a small fraction of the speed of the other unsymmetrically substituted dienines, which contained smaller aliphatic radicals (for example, methyl and ethyl groups). A similar hindrance to the hydration of dienines as a result of the screening of the triple bond by aromatic and large aliphatic radicals has also been noted previously in our laboratory in an entire series of other examples (5-propyl-1,5-octadien-3-ine, 5-methyl-1,5-tetradecadien-3-ine, 5,6-diphenyl-1,5-hexadien-3-ine, [5], and others).



The dienone (IV), upon hydrogenation in a solution of methanol with Pt catalyst, absorbed two molecules of hydrogen, and was converted into 5-tert. butyl-6-methylheptan-4-one (VII). During this process the first hydrogen molecule, which corresponded to the hydrogenation of the allyl radical of the dienone (IV) was added very rapidly, and then the hydrogenation of the considerably branched vinyl radical slowed down sharply (to 1/15th or 1/20th), and was competed only after many hours of shaking. The same sharply stepwise character of hydrogenation was also observed in our laboratory in the case of 5-isopropyl-6-methyl-1,5-heptadien-4-one, where the substituted allyl radical was also hydrogenated rapidly, and the completely substituted and strongly branched vinyl radical was hydrogenated with extreme difficulty, and under ordinary conditions could not even be

hydrogenated at all, [1].

The cyclopentenone (V), like the other cyclopentenones similar to it, which contained only a single substituent (the methyl group) at the double bond in the ring, was hydrogenated with Pt catalyst even in methanol solution with ease, and was thus smoothly converted into the corresponding saturated cyclic ketone, 1-tert.-butyl-2,2,3-trimethylcyclopentan-5-one (VIII).

The structure of the cyclopentenone (V) was also confirmed by means of ozonation, giving as a result formic acid and α -tert.-butyl- β , β -dimethyllevulinic acid (IX), which upon oxidation with alkali and bromine was smoothly converted into α , α -dimethyl- α '-tert.-butylsuccinic acid (X).

As a result of the difficulty of hydrating the dienine (III), it was converted directly into the cyclopentenone (V) by heating with phosphoric acid, but only a small yield (about 10%) was obtained.

EXPERIMENTAL

The preparation of pentamethylacetone. To 120 g of finely ground sodium-amide, 500 ml of absolute ether was added, and over a period of an hour, 250 g of diisopropyl ketone (b.p. 124-125°) was added with continuous stirring. The mixture was then heated for 4 hours with vigorous boiling of the ether until the evolution of ammonia had completely ceased. To the cooled reaction mixture there was added, drop by drop over a period of an hour, 380 g of methyl iodide. After this, the stirring was continued, with vigorous boiling of the ether, for an additional 2 hours. The sodium iodide which precipitated was dissolved in water (200 ml), the ether layer separated, neutralized with carbon dioxide, dried over calcined magnesium sulfate, and the ether driven off and the residue distilled. 155 g of pentamethylacetone was obtained, with a boiling point of 134-135° (745 mm) [6].

The synthesis of isopropyl-tert.-butylvinylethynyl carbinol. To an ether solution of vinylacetylenyl magnesium bromide which was prepared from 60 g of magnesium, 275 g of ethyl bromide, 140 g of vinylacetylene and 500 ml of absolute ether, 210 g of pentamethylacetone was added drop by drop over a period of an hour, with continuous stirring. The reaction mixture was then stirred for an additional 2 hours at a temperature of 40°, and was allowed to stand overnight. On the next day, 0.5 g of hydroquinone was added, and while the mixture was cooled with ice water and stirred vigorously, 500 ml of 15% hydrochloric acid was added drop by drop. The ether layer was separated, the aqueous layer extracted with ether, the product dried with magnesium sulfate, and after the ether had been driven off, the residue was fractionated in vacuum. 230 g of isopropyl-tert.-butylvinylethynyl carbinol (I) was obtained:

B.p. 79-79.2° at 6 mm; n_D^{20} 1.4782; d_4^{20} 0.8880; MR_D found 57.35; computed 56.65.

7.930 mg substance: 23.200 mg CO₂; 7.757 mg H₂O.

5.230 mg substance: 15.280 mg CO₂; 5.190 mg H₂O.

Found %: C 79.85, 79.73; H 10.94, 11.10.

C₁₂H₂₀O. Computed %: C 79.85; H 10.76.

The hydrogenation of isopropyl-tert.-butylvinylethynyl carbinol. 4.2 g of the carbinol (I) was hydrogenated with Pt catalyst in a solution of 10 ml of glacial acetic acid. The hydrogenation took place rapidly and was complete after 4 hours with the absorption of 1600 ml of hydrogen (3 mol.). The substance was dissolved in ether, washed with a solution of sodium bicarbonate, dried with calcined magnesium sulfate, and after the ether had been driven off, was fractionated in vacuum. 2.8 g of isopropylbutyl-tert-butyl carbinol (II) was obtained.

B.p. 79° at 6 mm; n_D^{20} 1.4578, d_4^{20} 0.8565; MR_D found 59.14, computed 59.12.

12.74 mg substance: 36.27 mg CO_2 ; 15.09 mg H_2O .

13.35 mg substance: 37.92 mg CO_2 ; 15.52 mg H_2O .

Found %: C 77.69, 77.52; H 13.25, 13.05.

$C_{12}H_{26}O$. Computed %: C 77.40; H 13.97.

The dehydration of isopropyl-tert.-butylvinylethynyl carbinol. A mixture of 200 g of the carbinol (I) and 250 g of phosphoric acid (sp. gr. 1.705) was stirred for 30 minutes at room temperature and for 1 hour at 60-65°. The product was diluted with water, extracted with ether, neutralized with sodium bicarbonate, and dried with calcined magnesium sulfate. After the ether had been driven off, and a careful vacuum fractionation carried out, 120 g of 5-tert.-butyl-6-methyl-1,5-heptadien-3-ine (III) was obtained. This had the following constants:

B.p. 62.5-63° at 6.5 mm; n_D^{20} 1.4805; d_4^{20} 0.8250; MR_D found 56.0, computed 54.67.

4.972 mg substance: 16.130 mg CO_2 ; 4.935 mg H_2O .

4.410 mg substance: 14.320 mg CO_2 ; 4.400 mg H_2O .

Found %: C 88.53, 88.61; H 11.11, 11.12.

$C_{12}H_{18}$. Computed %: C 88.88; H 11.12.

The dienine (III) was a colorless liquid with a pleasant conifer odor. It quickly polymerized to give a fine film in the air, and slowly polymerized in a sealed ampoule. In addition to the dienine (III), this experiment also gave 5.2 g of the 1-tert.-butyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one described below, in the form of a light-yellow liquid with a honey odor, b.p. 90-92° at 6 mm; $n_D^{18.5}$ 1.4807.

The hydrogenation of 5-tert.-butyl-6-methyl-1,5-heptadien-3-ine. 3.2 g of the dienine (III) was hydrogenated in the presence of Pt catalyst in a solution of 20 ml of methanol. In a period of 3 hours, 1330 ml of hydrogen (3 mol.) were absorbed. The methanol was driven off and the substance fractionated in vacuum. 2.8 g of 5-tert.-butyl-6-methyl-5-heptene (VI) was obtained. The substance immediately decolorized a solution of bromine in chloroform.

B.p. 75-75.5° at 11 mm; $n_D^{18.5}$ 1.4425; d_4^{20} 0.795; MR_D found 56.12, computed 57.13.

9.79 mg substance: 30.29 mg CO_2 , 12.69 mg H_2O .

15.20 mg substance: 46.97 mg CO_2 , 19.31 mg H_2O .

Found %: C 84.44, 84.33; H 14.41, 14.21.

$C_{12}H_{24}$. Computed %: C 85.71; H 14.29.

The cyclization-hydration of 5-tert.-butyl-6-methyl-1,5-heptadien-3-ine. A mixture of 20 g of the dienine (III) and 20 ml of phosphoric acid (sp. gr. 1.735) was stirred for 30 minutes at a temperature of 60-65°. The product was diluted with water, extracted with ether, neutralized with a solution of sodium bicarbonate, dried with magnesium sulfate, and after removal of the ether, fractionated in vacuum. 2 g of the original dienine were obtained, and in addition, 2 g of the 2,2,3-trimethyl-1-tert.-butyl- $\Delta^{3,4}$ -cyclopenten-5-one (V) described below, with b.p. 90-92° at 6 mm; $n_D^{18.5}$ 1.4807. The rest of the material tarred.

The hydration of 5-tert.-butyl-6-methyl-1,5-heptadien-3-ine. A mixture of 600 ml of 90% methanol, 1 g of concentrated sulfuric acid, 1 g of mercuric sulfate, and 115 g of the dienine (III) was vigorously stirred at 65° for 12 hours. During this period, after every hour an additional amount of 0.5 g of mercuric sulfate was added. The methanol was driven off in a vacuum of 120 mm, and the product diluted with water, extracted with ether, neutralized with sodium bicarbonate, and dried with magnesium sulfate. After the ether had been driven off, the substance was fractionated in vacuum. 72 g of the dienine was recovered (b.p. 62° at 6 mm), and 31 g of a fraction with boiling range 78 to 119° at 6 mm. This was distilled

twice with p-toluenesulfonic acid (0.2% in a vacuum of 70 mm at a bath temperature of 170°. As a result of the fractionation, 5 g of 5-tert.-butyl-6-methyl-1,5-heptadien-4-one (IV) was obtained in the form of a light yellow oil with a pleasant odor.

B.p. 77-80° at 6 mm; n_D^{20} 1.4717; d_4^{20} 0.8860; MR_D found 56.95; computed 56.67.

3.895 mg substance: 11.382 mg CO₂; 3.845 mg H₂O.

6.070 mg substance: 17.724 mg CO₂; 5.930 mg H₂O.

Found %: C 79.75, 79.70; H 11.04, 10.93.

C₁₂H₂₀O. Computed %: C 79.85; H 10.76.

The carbonyl derivatives of this dienone could not be obtained. In addition to the dienone (IV), this experiment also gave 22 g of a fraction with boiling range 74-108° at 6 mm; n_D^{20} 1.4735, consisting of the dienone (IV) and the methoxy ketone which corresponded to it. When this was treated with phosphoric acid, as described below, the cyclopentenone (V) was obtained.

The cyclization of 5-tert.-butyl-6-methyl-1,5-heptadien-4-one. 22 g of the fraction described above (b. range 74-108° at 6 mm, n_D^{20} 1.4735) was mixed with 30 ml of phosphoric acid (sp. gr. 1.7). Heat was evolved, and the temperature rose to 45°. The substance was stirred for 30 minutes at room temperature and 45 minutes at 65°, diluted with water, extracted with ether, washed with a solution of sodium bicarbonate, dried with magnesium sulfate, and after removal of the ether, fractionated in vacuum. 9 g of 2,2,3-trimethyl-1-tert.-butyl- $\Delta^{3,4}$ -cyclopenten-5-one (V) was obtained in the form of a light-yellow oil with a honey odor.

B.p. 90-93° at 6 mm; n_D^{20} 1.4780; d_4^{20} 0.9231; MR_D found 55.1; computed 54.5.

5.308 mg substance: 15.293 mg CO₂; 5.180 mg H₂O.

5.150 mg substance: 14.782 mg CO₂; 5.075 mg H₂O.

Found %: C 78.63, 78.33; H 11.17, 11.03.

C₁₂H₂₀O. Computed %: C 79.85, H 10.76.

The semicarbazone and 2,4-dinitrophenylhydrazone of this cyclic ketone could not be obtained. In addition, this experiment also gave 6 g of a fraction with b.p. 93-97° at 6 mm, n_D^{20} 1.4784; this was also chiefly the cyclopentenone (V).

The hydrogenation of 5-tert.-butyl-6-methyl-1,5-heptadien-4-one. 2.4 g of the dienone (IV) (b.p. 77-80° at 6 mm; n_D^{20} 1.4717) was hydrogenated in a solution of 20 ml of methanol with Pt catalyst. 560 ml of hydrogen (2 mol.) were absorbed, 290 ml of hydrogen being absorbed in 1.5 hours, the rest by the end of 22 hours. Fractional distillation of the product gave 1.3 g of 5-tert.-butyl-6-methyl-heptan-4-one (VII).

B.p. 70-72° at 6 mm; $n_D^{19.5}$ 1.4455; d_4^{20} 0.8476; MR_D found 57.78; computed 57.61.

3.060 mg substance: 8.776 mg CO₂; 3.500 mg H₂O.

Found %: C 78.26; H 12.83.

C₁₂H₂₄O. Computed %: C 78.22, H 13.03.

The hydrogenation of 2,2,3-trimethyl-1-tert.-butyl- $\Delta^{3,4}$ -cyclopenten-5-one. 2.06 g of the cyclopentenone (V) were hydrogenated with Pt catalyst in a solution of 20 ml of methanol. After 2 hours, 245 ml of hydrogen (1 mol.) was absorbed. The catalyst was coagulated, and the hydrogenation cut short. The methanol was driven off, and the substance distilled in vacuum. 1.3 g of 2,2,3-trimethyl-1-tert.-butylcyclopentan-5-one (VIII) was obtained in the form of a pleasant-smelling colorless oil. The carbonyl derivatives of the cyclic ketone (VIII) could not be obtained.

B.p. 87-89° at 6 mm; $n_D^{19.5}$ 1.4592; d_4^{20} 0.8915; MR_D found 55.6, computed 55.41.

3.445 mg substance: 9.957 mg CO_2 ; 3.616 mg H_2O .

4.731 mg substance: 13.683 mg CO_2 ; 5.017 mg H_2O .

Found %: C 78.86, 78.83; H 11.74, 11.86.

$C_{12}H_{22}O$. Computed %: C 79.10; H 12.09.

The ozonation of 2,2,3-trimethyl-1-tert.-butyl- $\Delta^{3,4}$ -cyclopenten-5-one. 4.2 g of the cyclopentenone (V) in a solution of 30 ml of chloroform was ozonized with oxygen which contained 6% of ozone over a period of 10 hours, at a velocity of 4 liters per hour. The ozonides were hydrolyzed by vigorous stirring with 50 ml of water for 3 hours at 60-65°, and 8 ml of perhydrol was then added, and the stirring continued at the same temperature for an additional 2 hours. The acids were neutralized with 12 g of sodium bicarbonate, and the neutral products were extracted with ether, there was almost nothing of them. From 1/35th of the aqueous solution of organic acids, 0.1360 g of calomel was obtained. This corresponded to a total content of 0.47 g of formic acid in the solution (44% of theory). The solution of salts of organic acids was evaporated to dryness, the salts decomposed with concentrated hydrochloric acid (15 ml) and the organic acids were extracted with ether and dried with sodium sulfate. A fractional distillation gave 0.55 g of formic acid (b.p. 97-102°) and 1.2 g of α -tert.-butyl- β,β -dimethyllevulinic acid (IX) in the form of an extremely viscous yellowish green liquid with b.p. 124-125° at 1.5 mm; n_D^{20} 1.4566. The 2,4-dinitrophenylhydrazone of this acid was obtained by heating the reagents in alcoholic solution for 8 hours at 80°, and subsequent standing for 2 days. It was in the form of a light yellow powder, which melted without decomposition at 194° (from alcohol).

3.710 mg substance: 0.510 ml N_2 (22°, 743 mm).

3.790 mg substance: 0.517 ml N_2 (22°, 750 mm).

Found %: N 15.59, 15.56.

$C_{17}H_{24}O_5N_4$. Computed %: N 14.74.

The oxidation of α -tert.-butyl- β,β -dimethyllevulinic acid. 0.85 g of the ketoacid (IX) was dissolved in 27 ml of 10% caustic soda and 3 g of bromine was added, while the mixture was cooled with ice water. The liquid was stirred for 2 hours at room temperature, the solution filtered, acidified with 14 ml of 15% hydrochloric acid, and evaporated to dryness. Upon standing, 0.55 g of α,α -dimethyl- α' -tert.-butylsuccinic acid (X) precipitated from the solution. After three recrystallizations from water, this melted at 138°.

3.577 mg substance: 7.596 mg CO_2 ; 2.811 mg H_2O .

4.050 mg substance: 8.587 mg CO_2 ; 3.185 mg H_2O .

Found %: C 57.95, 57.86; H 8.79, 8.80.

$C_{10}H_{18}O_4$. Computed %: C 59.35; H 8.91.

0.266 g acid: 26.25 ml 0.1 N NaOH.

Found: M 203.8.

$C_{10}H_{18}O_4$ Computed: M 202.

SUMMARY

The action of vinylacetylenyl magnesium bromide on pentamethylacetone gave an approximately 90% yield of isopropyl-tert.-butyl-vinylethynyl carbinol (I), which was hydrogenated with Pt catalyst to give isopropyl-n-butyl-tert.-butyl-carbinol (II).

Dehydration of the carbinol (I) by means of phosphoric acid gave in approximately 70% yield 5-tert-butyl-6-methyl-1,5-heptadien-3-ine (III), which upon hydrogenation with Pt catalyst under ordinary conditions absorbed only 3 molecules of hydrogen and gave the olefin (VI). When the diene (III) was hydrated in

aqueous solutions of methanol in the presence of sulfuric acid and mercuric sulfate, 5-tert.-butyl-6-methyl-1,5-heptadien-4-one (IV) was formed. Under the influence of phosphoric acid, this was easily cyclized to 1-tert.-butyl-2,2,3-trimethyl- $\Delta^{3,4}$ -cyclopenten-5-one (V). The hydrogenation of the dienone (IV) with Pt catalyst had a sharply stepwise character, the unsubstituted allyl radical being hydrogenated very rapidly, while the fully substituted and strongly branched vinyl radical was hydrogenated with extreme slowness.

The hydrogenation of the cyclopentenone (V) with Pt catalyst took place easily, and smoothly gave 1-tert.-butyl-2,2,3-trimethylcyclopentan-5-one (VIII). The structure of the cyclopentenone (V) was confirmed by its ozonation to give α -tert.-butyl- β,β -dimethyllevulinic acid (IX), which was then oxidized by alkaline bromine to give α,α -dimethyl- α' -tert.-butylsuccinic acid (X).

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* See CB translation p. a-331 ff.

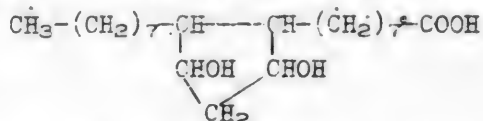
** See CB translation p. 1501 ff.

THE CONDENSATION OF OLEIC ACID WITH FORMALDEHYDE

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In 1911 Fokin [1] published a paper on the condensation of unsaturated acids (undecylenic, oleic, and elaidic) with formaldehyde. Fokin showed that the condensation was accompanied by the disappearance of the double bond. In particular, the condensation of oleic acid was accompanied by the formation of three products, of which one was a crystalline substance with m.p. 112-114°, and the composition $C_{21}H_{40}O_4$. To this last, Fokin ascribed the structure:



The proposed structure of the condensation product was based on the elementary analysis, on the number of hydroxyl groups found by the method of acetylation, and on the molecular weight by titration. There is no doubt that this investigation was of great interest. In case of confirmation, it would have revealed the possibility of obtaining acids with a higher degree of unsaturation by utilizing dehydration.

The purpose of our investigation was to elucidate the structure of the crystalline product. The substance which we obtained, in accordance with Fokin's directions, melted at 116-117°. The elementary analysis, by Liebig's method, confirmed the formula $C_{21}H_{40}O_4$ proposed by Fokin. However, further investigation gave results that contradicted his.

The compound contained one alcohol group, which was confirmed by the determination of hydroxyls by the Chugaev-Tserevitinov method, and by the method of acetylation under the conditions used by Fokin. The incorrectness of the results he had obtained could be explained by the presence of acid anhydrides which remained undecomposed to the end. These were formed by the action of acetic anhydride on the original substance.

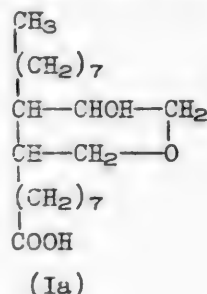
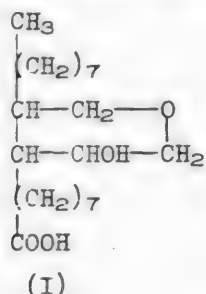
A further study of the crystalline compound confirmed our results. The ester $C_{20}H_{38}O_2\text{COOC}_2\text{H}_5$ was synthesized in the usual manner from ethyl alcohol and the acid. It was a crystalline substance with m.p. 69-70°. Analysis of the substance by Liebig's method, and an ebullioscopic determination of the molecular weight, confirmed the formula $C_{23}H_{44}O_4$. The presence of a single hydroxyl group was detected by the Chugaev-Tserevitinov method.

The work which had been done on the study of the structure of the compound $C_{20}H_{38}O(\text{OH})\text{COOH}$ left it unclear in what sort of functional group the second oxygen atom was. Attempts to obtain derivatives from a carbonyl group (the oxime, semi-

carbazone, phenylhydrazone) did not give positive results. In addition, there was no alkoxyl group.

The only thing left to assume was that the oxygen atom formed part of a ring, and that we had a six-membered heterocycle, and not a five-membered one, as Fokin had proposed^{*}.

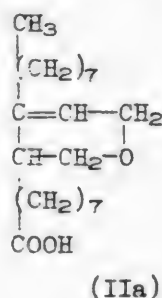
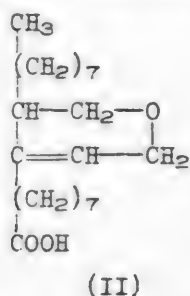
It seemed that most probably the condensation product of oleic acid and formaldehyde could be assigned one of the two formulas written below, (I) or (Ia):



The secondary nature of the alcohol group was deducible from the formation of the ketone $\text{C}_{19}\text{H}_{37}\text{O}(\text{CO})\text{COOH}$ with m.p. $64-65^\circ$ by oxidation with chromic anhydride. The latter was characterized by a number of derivatives. The oxime $\text{C}_{21}\text{H}_{39}\text{O}_4\text{N}$ was synthesized, as well as the semicarbazone $\text{C}_{22}\text{H}_{41}\text{O}_4\text{N}_2$, with m.p. $146-147^\circ$. Finally, the ester of the keto acid with m.p. $25-27^\circ$ was also studied.

We must observe that the keto acid and its ester were partially enolized, the latter to a somewhat greater extent. While the determination of the hydroxyl number of the keto acid gave 1.16 hydroxyls, the ether, which was not supposed to contain an alcohol group, gave 0.48 hydroxyl. In order further to elucidate the position of the alcohol group and of the oxygen bridge, the original heterocyclic monohydroxy acid was dehydrated by various methods: by means of the chloro derivatives, with the subsequent splitting off of hydrogen chloride with alcoholic alkali, by the direct dehydration of the hydroxyacid with phosphoric anhydride, and by the pyrolysis of the hydroxyacid. In all three cases, one and the same unsaturated acid was obtained. This was an almost colorless, fairly mobile liquid with b.p. about 240° (0.10 to 0.14 mm pressure), which did not crystallize in the cold, and had a high specific gravity (d_4^{20} 0.9711):

If we start with the formulas indicated above for the heterocyclic hydroxyacid, then the probable structure of the unsaturated acid will be expressed by one of the following formulas (II) and (IIa):

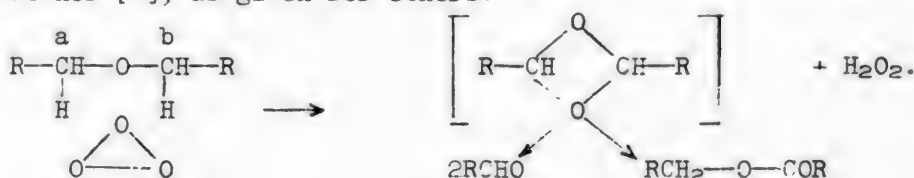


* We were forced to assume the presence of a ring, instead of the addition of open chains at the position of the double bond. This was indicated both by the properties of the crystalline compound, as mentioned above, and by the data (see below) of oxidation with chromic anhydride, which resulted in a stable ketone. It would have been incomprehensible also if ozonization of an unsaturated acid had given compounds with the composition $\text{C}_{18}\text{H}_{34}\text{O}_4$ and $\text{C}_{18}\text{H}_{36}\text{O}_4$.

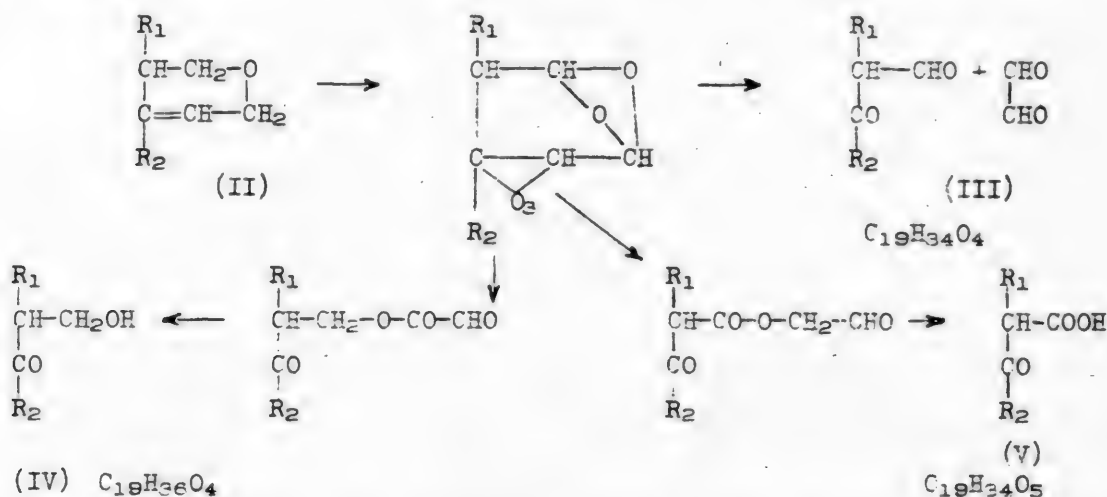
** For oleic acid d_4^{20} is 0.895.

The unsaturated acid forms a barium salt with the composition $(C_{21}H_{13}O_3)_2Ba$. The acid is hydrogenated very slowly. Hydrogenation by means of Raney catalyst is concluded after 8 days. Hydrogenation also took place slowly in the presence of platinum black. The hydrogenation product, $C_{21}H_{40}O_3$, was a liquid which in appearance differed little from the original unsaturated acid, but did not give any reactions for the double bond. After several months, crystals precipitated out of the oily liquid. These were white mother-of-pearl leaves with m.p. 39.5-40°. The elementary composition of both the crystals and the liquid portion was the same, $C_{21}H_{40}O_3$. Apparently the two substances were cis and trans isomers.

Upon ozonation, two molecules of ozone reacted with the unsaturated acid. A sharp difference was noted in the velocity of the reaction. While the first molecule of ozone reacted in a period of 22 minutes, the second molecule took 171 minutes. There is no doubt that the double bond reacted first, to form an ozonide. Fischer has shown that the ozonization of ethers takes place much more slowly than the ozonization of unsaturated compounds. The oxygen bridge, when subjected to the action of ozone, apparently reacts in accordance with the equations of Fischer [2], as given for ethers.



In accordance with this equation, two oxygens from the molecule of ozone plus two hydrogens of the ether form hydrogen peroxide. Then the reaction takes place in two directions: 1) with the formation of two molecules of aldehyde, and 2) with the formation of an ester, which is obtained as the result of the transfer of an atom of hydrogen from a to b, or the other way around. Depending on the character of the radical, the first or the second direction will prevail. Taking into account these ideas of Fischer's, we can expect the following products of reaction:



In a similar manner, upon ozonation, formula (IIa) can give three substances of analogous structure. The ozonide obtained appeared very stable. Neither heating with water nor treatment with steam resulted in the complete decomposition of the ozonide.

The decomposition of the ozonide gave three products: 1) an acid which

We designate the radical $\text{CH}_3-(\text{CH}_2)_7$ by R_1 , the radical $(\text{CH}_2)_7-\text{COOH}$ by R_2 .

could not be steam distilled (the main product); 2) an acid which was steam distilled, 3) an aqueous solution of distillate, which contained a volatile aldehyde, reacting with fuchsine-sulfurous acid and an ammoniacal solution of silver oxide.

The elementary analysis and the molecular weight of the acid which did not distil over with steam were close to two formulas: a ketoaldehyde acid $C_{19}H_{34}O_4$, and a ketohydroxy acid $C_{19}H_{36}O_4$. A more detailed study of the chief product of ozonolysis showed that it was actually a mixture of these two substances. Two semicarbazones were obtained, one crystalline, with m.p. 229-229.5°, the other liquid.

The nitrogen content in the crystalline semicarbazone corresponded to the presence of two carbonyl groups, of which one was a keto group and the other an aldehyde. Therefore, we had obtained a disemicarbazone $C_{17}H_{34}O_2(C=N-NHCONH_2)_2$, corresponding to the ketoaldehyde acid $C_{19}H_{34}O_4$.

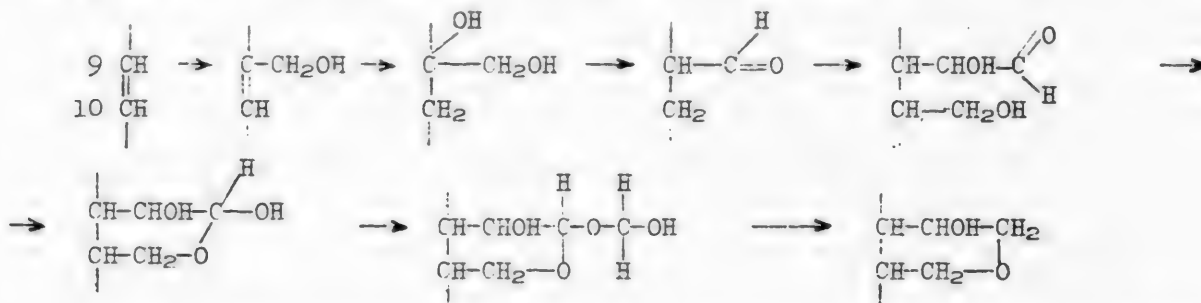
The nitrogen content in the liquid semicarbazone corresponded to one carbonyl group. The oil, therefore, was the monosemicarbazone $C_{18}H_{36}O_3(C=N-NHCONH_2)$, as contrasted with the crystalline disemicarbazone.

Apparently, the monosemicarbazone corresponded to the ketohydroxy acid $C_{19}H_{34}O_4$, which could be formed on an equal footing with the ketoaldehyde acid according to Fischer's equations.

The results of a study of the ozonation products confirmed the suggested formula of the unsaturated acid (II) or (IIa). Therefore, it was more probable that the heterocyclic hydroxyacid which had been synthesized could be assigned one of the two formulas (I) or (Ia).

It now remained unclear according to what mechanism the reaction between the oleic acid and the formaldehyde took place in the presence of sulfuric acid.

Taking into account the investigations of Prins [3] and Langlois [4], we can picture the reaction mechanism in the following manner.



The first reaction phase takes place according to the mechanism of Prins and Langlois with the formation of an unsaturated alcohol. The next phase is hydration with the formation of a glycol, which is immediately transformed into an aldehyde with the evolution of water. Then two molecules of formaldehyde add on: the first substituting one atom of hydrogen on the tenth carbon atom by CH_2OH , the second condensing with the aldehyde group. The alcohol and aldehyde groups now present, under acid conditions, form a cyclic acetal, which with the next molecule of formaldehyde gives an unstable compound. This decomposes with the separation of formic acid and the substance first taken into consideration.

EXPERIMENTAL

The condensation of oleic acid with formaldehyde

In the first experiments, the oleic acid required for the condensation was isolated from almond oil or apricot oil and subjected to careful purification

from saturated acids (by means of the lead salts) and from linoleic acid (by crystallization from acetone). In the later experiments, the acids obtained from the oils mentioned were directly subjected to the action of formaldehyde. The condensation of formaldehyde with oleic acid took place in the following manner. To 100 ml of formalin (36-38%) there was added with cooling (to about -17°) in 3 or 4 portions, 150 ml of sulfuric acid (sp. gr. 1.84). During this addition, the temperature of the reaction mixture rose to 35° . The temperature was brought down to -8 or -10° , and from a dropping funnel the oleic acid (100 g) was slowly added, over a period of one and a half hours, with constant stirring. The temperature of the mixture did not rise above 5° . At the end of the addition of the acid, the temperature of the mixture was allowed to rise to room temperature. The mixture was stirred for four days, the first day at 15° , the other three days at $40-50^{\circ}$. The reaction mixture consisted of two layers: the upper was yellow and viscous, (the condensation product) and the lower was fluid. The contents of the reaction flask were poured into a beaker with 500 ml of a solution of table salt in water. This changed the condensation product into a light brown mass, which was removed from the liquid portion and heated for an hour with 2% H_2SO_4 and a solution of NaCl in order to remove formaldehyde polymers. The light dough-like mass was then washed with an aqueous solution of sodium chloride to remove sulfuric acid and formalin. The dough-like mass was placed in a two-liter bottle and shaken with 400 ml of petroleum ether for 3 hours. The petroleum ether was filtered off and a fresh portion of ether poured over the residue and again shaken. This extraction was repeated 7 times."

After the petroleum ether was driven off, 72 g of a viscous yellowish liquid was obtained. The residue insoluble in petroleum ether was treated with 500 ml of ethyl ether. This produced a voluminous white precipitate, which was filtered off after standing for a day, and recrystallized from alcohol and ether. The condensation of an additional 650 ml of oleic acid was carried out in a similar manner. The yield of solid substance was 25 g (3.8%). The final portions of the crystalline compound were obtained directly from the mixture of acids after saponifying the oil. The condensation product was treated with water and dissolved in ethyl ether. The precipitate that formed was filtered off and purified as indicated above. From 900 g of acid, 24 g of the substance was obtained. The melting point of the original substance obtained was in all cases $116-117^{\circ}$; the hardening temperature was $112-110^{\circ}$.

Investigation of the crystalline compound with m.p. $116-117^{\circ}$.

0.0800 g substance: 0.2071 g CO_2 , 0.1018 g H_2O .
 0.0949 g substance: 0.2458 g CO_2 , 0.0974 g H_2O .
 Found %: C 70.60, 70.65; H 11.36, 11.40.
 $C_{21}H_{40}O_4$. Computed %: C 70.78, H 11.23.
 0.1636 g substance: KOH consumed 0.0258 g.
 0.1636 g substance: KOH consumed 0.0258 g.
 Found: M 355.7, 355.7.
 $C_{21}H_{40}O_4$. Computed: M 356.0.
 0.0500 g substance: 5.7 ml CH_4 (0° , 760 mm) (Chugaev-Tserev-
 0.0502 g substance: 5.8 ml CH_4 (0° , 760 mm). itinov).
 Found OH number: 1.83, 1.85.

Determination of the number of alcoholic hydroxyl groups by acetylation. ***

1.8768 g substance: KOH consumed for neutralization of acetic acid 0.3040 g.
 0.5016 g substance: KOH consumed for neutralization of acetic acid 0.0811 g.
 0.5614 g substance: KOH consumed for neutralization of acetic acid 0.0761 g.
 Found OH number: 1.17, 1.17, 0.98

The sulfuric acid had to be added as rapidly as possible in order to avoid the formation of polymers of formaldehyde which would impede further reaction.

In the later experiments the extraction was carried out in a Soxhlet apparatus.

The acetic acid was distilled with steam from the saponified acetylation product before titrating.

The preparation of the ethyl ester $C_{20}H_{39}O_2COOC_2H_5$ with m.p. 70-71°

6.8 g of the original substance was dissolved in 70 ml of a 5% solution of hydrogen chloride in absolute ethyl alcohol. The reaction mixture was heated with a reflux condenser for 5 hours. Then water containing the calculated amount of soda solution was added to the solution which was to be neutralized. The ethyl ester which precipitated was filtered off and recrystallized from alcohol and petroleum ether. 6.5 g (88%) was obtained.

The ethyl ester was a white powder with m.p. 70-71° and hardening temperature 70-68°. It was very soluble in ether, acetone, and xylene.

0.0989 g substance; 0.2596 g CO_2 ; 0.1017 g H_2O .

0.1036 g substance; 0.2723 g CO_2 ; 0.1063 g H_2O .

Found %: C 71.58, 71.68; H 11.43, 11.46.

$C_{23}H_{44}O_4$. Computed %: C 71.85; H 11.46.

Determination of the molecular weight by ebullioscopy:

0.5704 g substance: 37.34 g solution: Δt 0.85°.

0.8875 g substance: 35.88 g solution: Δt 0.140°.

Found: M 388, 381.6.

$C_{23}H_{44}O_4$. Computed: M 384.

Determination of hydroxyl groups (Chugaev-Tserevitinov):

0.1600 g substance: 9.0 ml CH_4 (0°, 760 mm).

0.1688 g substance: 9.8 ml CH_4 (0°, 760 mm).

0.0830 g substance: 4.7 ml CH_4 (0°, 760 mm).

Found OH number: 0.97, 1.02, 0.98.

The Synthesis of the heterocyclic keto acid $C_{19}H_{37}O(CO)COOH$ with m.p. 64-65°

The oxidation of the original substance, $C_{21}H_{40}O_4$, with m.p. 116-117°, was effected in the following manner: 15 g of the substance was dissolved with heating in 150 ml of glacial acetic acid. After cooling to room temperature, 7.5 g of CrO_3 was added, with stirring, in portions. The reaction mixture heated up. It was cooled and through it, for a period of an hour, there was passed a stream of sulfur dioxide in order to reduce the unreacted chromic anhydride. The hydrochloric acid was added in an amount sufficient to change the Cr_2O_3 formed into $CrCl_3$, along with 300 ml of water.

Upon the addition of water, a white precipitate formed. This was filtered off and washed with water. In order to complete the removal of traces of chromium, the precipitate was treated during heating, with a 5% solution of caustic potash. The potassium salt of the oxidation product which formed went into solution, which was filtered while hot. When the filtrate was acidified with hydrochloric acid, a white precipitate formed. This was filtered off and recrystallized from petroleum ether. The product obtained was a white powder with m.p. 64-65°, hardening temperature 58-57°. It was very soluble in alcohol and in ether. Yield 9 g.

0.1018 g substance. 0.2658 g CO_2 ; 0.0985 g H_2O .

0.0967 g substance. 0.2521 g CO_2 ; 0.0936 g H_2O .

0.0954 g substance. 0.2486 g CO_2 ; 0.0927 g H_2O .

Found %: C 71.21, 71.10, 71.07; H 10.75, 10.76, 10.79.

$C_{21}H_{38}O_4$. Computed %: C 71.19; H 10.74.

Determination of the molecular weight by titration:

0.1216 g substance. KOH consumed 0.01934 g.

0.1484 g substance. KOH consumed 0.02363 g.

Found: M 352.8, 352.3.

$C_{21}H_{38}O_4$. Computed: M 354.

Determination of the number of hydroxyl groups (Chugaev-Tserevitinov)

0.0880 g substance: 6.6 ml CH₄ (0°, 760 mm).

0.0980 g substance: 7.2 ml CH₄ (0°, 760 mm).

0.1036 g substance: 7.5 ml CH₄ (0°, 750 mm).

Found OH : 1.19, 1.16, 1.14.

The results of analysis show the presence of an excessive amount of hydroxyls; this may be explained by partial enolization. This explanation is confirmed by a positive reaction with FeCl₃ in alcoholic solution.

The preparation of the oxime C₁₉H₃₇O(C=NOH)COOH of the ketoacid

The preparation of the oxime was effected by heating the alcoholic solution of the ketone with hydroxylamine hydrochloride. 0.75 g of the ketoacid was used, with 0.50 g of hydroxylamine hydrochloride, and 1.5 g of KOH. After the heating, the alcohol was driven off, and the residue dissolved with stirring in 30 ml of water and acidified with hydrochloric acid. The floating waxy substance was extracted with ether. The ether solution was dried with Na₂SO₄. After the ether had been driven off, the residue was an oil with a straw color. After 5 or 6 days, a small amount of crystals appeared, but because of the minuteness of the quantity they could not be separated. 0.68 g of the liquid oxime was obtained.

0.0890 g substance: consumed H₂SO₄ 0.01176 g (Kheldahl)

0.0890 g substance: consumed H₂SO₄ 0.01152 g.

0.0893 g substance: consumed H₂SO₄ 0.0119 g.

Found %: N 3.78, 3.70, 3.61.

C₂₁H₃₉O₄N. Computed %: N 3.84.

The preparation of the semicarbazone C₁₉H₃₇O(C=N-NH-CO-NH₂)COOH

0.42 g of semicarbazide hydrochloride and 0.4 g of potassium acetate were dissolved in 1 ml of water and mixed with a solution of 0.5 g of the ketoacid in alcohol. The solution was allowed to stand for two weeks. The transparent solution was concentrated to 1/4th its volume (in vacuum). A precipitate formed in the remaining solution. This was filtered off, washed with alcohol, and recrystallized from ether. A white powder was obtained with m.p. 146-147°.

0.0405 g substance: consumed 0.01446 g H₂SO₄.

0.0405 g substance: consumed 0.01457 g H₂SO₄.

Found %: N 10.20, 10.28.

C₂₂H₄₁O₄N₃. Computed %: N 10.22.

The preparation of the ethyl ester of the keto acid, C₁₉H₃₇O(CO)COOC₂H₅

The ethyl ester of the oxidation product was obtained in the same way as the ester of the original substance. After recrystallization from petroleum ether it was a white crystalline substance with m.p. 25-27°. The ester was partially enolized.

0.0924 g substance: 0.2444 g CO₂; 0.0908 g H₂O.

0.0816 g substance: 0.2158 g CO₂; 0.0805 g H₂O.

Found %: C 72.14, 72.12; H 10.92, 10.96.

C₂₃H₄₂O₄. Computed %: C 72.25; H 10.99.

0.1485 g substance: 4.30 ml CH₄ (0°, 760 mm).

0.0917 g substance: 2.45 ml CH₄ (0°, 760 mm).

0.0885 g substance: 2.40 ml CH₄ (0°, 760 mm).

Found OH: 0.50, 0.46, 0.47.

The preparation of the chloro derivative of the original substance with

m.p. 116-117°

5 g of the original substance was dissolved with heating in 50 ml of chloro-

form. The flask containing the solution was placed in cold water. Through a reflux condenser, 9 g of phosphorus pentachloride was added in portions, with stirring. At the end of the reaction the mixture was heated on the water bath for a half hour, and 10 ml of water was then added. The mixture was again heated on the water bath with stirring for 30 minutes. The chloroform was then driven off. The residue was dissolved in ethyl ether, washed free from acid with water, and dried over sodium sulfate. After the ether had been removed, 5 g of the chloro derivative was obtained in the form of an almost colorless transparent oil which did not crystallize in the cold.

0.2177 g substance. 0.0810 g AgCl (Stepanov).

0.2751 g substance. 0.1030 g AgCl.

Found %: Cl 9.21, 9.26.

$C_{21}H_{39}O_3Cl$. Computed %: Cl 9.48.

The preparation of the unsaturated cyclic acid $C_{21}H_{38}O_3$

To 35 g of the chloro-substituted $C_{21}H_{39}O_3Cl$, 93 ml of an alcoholic solution of caustic potash was added. The mixture was boiled on the water bath with a reflux condenser for 8 hours, and the alcohol was then driven off. The unsaturated acid which separated out was extracted with ethyl ether, washed with water, and dried. The acid which remained after the removal of the ether was subjected to distillation in a high vacuum. Yield 16 g. The unsaturated acid was an almost colorless, fairly mobile liquid with b.p. 240° (at 0.14 mm). An unsaturated acid with similar properties could be obtained by the dehydration of the hydroxyacid with phosphoric anhydride or by distillation in a vacuum of 23 mm. However, in this case the yield of acid was less.

0.1317 g substance. 0.3015 g CO_2 , 0.1337 g H_2O .

0.0964 g substance. 0.2040 g CO_2 , 0.0981 g H_2O .

Found %: C 74.86, 74.69; H 11.28, 11.31.

$C_{21}H_{38}O_3$. Computed %: C 74.56, H 11.33.

0.0908 g substance: 4.8 ml CH_4 (0° , 760 mm).

0.0748 g substance: 3.9 ml CH_4 (0° , 760 mm).

Found OH: 0.80, 0.80.

0.4160 g substance: consumed 0.0692 g KOH.

0.1924 g substance: consumed 0.0326 g KOH.

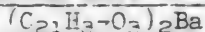
Found: M 337.2, 336.7.

$C_{21}H_{38}O_3$. Computed. M 338.

d_4^{18} 0.9729, d_4^{20} 0.9711, n_D^{20} 1.47616, MR_D 98.20.

$C_{21}H_{38}O_3$ F. Computed. MR_D 99.69.

The preparation of the barium salt of the unsaturated heterocyclic acid



1.25 g of the acid was dissolved in 40 ml of alcohol and neutralized with alkali, and then mixed, while being heated, with a hot alcoholic solution of barium chloride (2 g of $BaCl_2$ in 20 ml of 50% ethyl alcohol). The precipitated salt was dissolved in ether and washed with water. Upon the removal of the ether, the salt remained in the form of a vitreous mass which had no definite melting point. The salt was insoluble in alcohol, and dissolved in petroleum ether and in ethyl ether. It did not contain water of crystallization.

Determination of the barium content:

0.3272 g substance: 0.0920 g $BaSO_4$.

0.1947 g substance: 0.0546 g $BaSO_4$.

Found %: Ba 16.55, 16.51.

$(C_{21}H_{37}O_3)_2Ba$. Computed %: Ba 16.93.

The residue was dissolved in water and hydrochloric acid was added.

The Hydrogenation of the unsaturated heterocyclic acid

The hydrogenation was effected in the presence of Raney catalyst in alcohol solution. For purposes of hydrogenation, 1.35 g of the substance, 10 g of the catalyst, and 25 ml of alcohol were used. The absorption of hydrogen took place very slowly. In the first hour 20 ml were absorbed, in the second hour 7 ml, and from then on 1 or 2 ml per hour. Hydrogenation took place just as slowly in the presence of platinum black in ether solution. After the catalyst had been removed and the solvent driven off, the hydrogenation product was in the form of an oily liquid which gave no reaction for the double bond. After several months crystals precipitated from the oil in the form of white mother-of-pearl leaves, which were separated on a porous plate. M.p. 39.5-40°. The crystalline part and the liquid were analyzed. Their compositions were identical. Apparently, the two substances were cis and trans isomers.

Analysis of the substance with m.p. 39.5-40°.

0.0738 g substance: 0.2002 g CO₂; 0.0778 g H₂O.

0.0792 g substance: 0.2155 g CO₂; 0.0837 g H₂O.

Found %: C 73.98, 74.19; H 11.72, 11.74.

C₂₁H₄₀O₃. Computed %: C 74.12; H 11.77.

Analysis of the liquid portion:

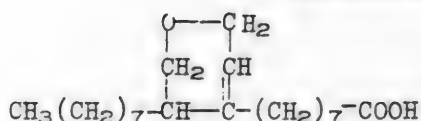
0.1346 g substance: 0.3654 g CO₂; 0.1418 g H₂O.

0.1472 g substance: 0.3992 g CO₂; 0.1557 g H₂O.

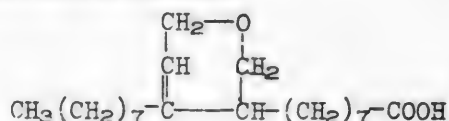
Found %: C 74.04, 73.95; H 11.71, 11.75.

C₂₁H₄₀O₃. Computed %: C 74.12; H 11.77.

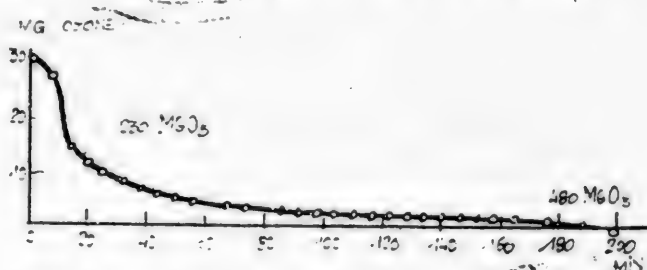
The ozonation of the unsaturated acid



or



1.62 g of the acid was dissolved in 60 g of chloroform. Oxygen which contained 5.5-6% of ozone was passed through the chloroform solution for 10 hours. During the ozonation the amount of ozone that had reacted was determined by the method of Brine and others, supplemented and completed by A.I. Yakubchik and N.G. Kasatkina. The results of the experiment are shown in the figure. The data show that two molecules of ozone (0.46 g) reacted. However, as can be seen from the curve, the velocities of reaction of the two molecules were different. While the first molecule of ozone (0.23 g) reacted in 22 minutes, the second required 171 minutes. A second ozonation experiment gave similar results.



The ozonation of the unsaturated acid

M = 338. Weight 1.62 g.

TABLE

Expt. No.	Weight of substance, g	Weight of ozonide	
		Found	Calculated
2	3.1	3.80	3.82
3	0.86	1.05	1.06

A comparison of the weights obtained and calculated shows that in addition to the two molecules of ozone, an additional one molecule of oxygen reacted.

The decomposition of the ozonide, after fruitless attempts by heating with water on a water bath, was accomplished by treatment with steam. The ozonide which remained undecomposed at the end was subjected to the action of alkali and heating for 11 hours. The reaction mixture was acidified with hydrochloric acid. The substances that were volatile with steam were distilled off, and the distillate was added to the first portion. The upper layer formed upon acidification was extracted with ether, washed with water, and dried. After the ether had been driven off, an oily yellow, non-crystallizing liquid was obtained.

The aqueous distillate was a solution with a pleasant odor, and contained floating drops of an oil which was extracted with ether. The ether solution was washed with water and dried. After the ether had been removed, there remained a liquid with a sharp odor. It gave no reaction with fuchsine-sulfurous acid, but easily dissolved in alkalis. The aqueous layer, after the removal of the oil, gave the characteristic aldehyde reaction with fuchsine-sulfurous acid and with an ammoniacal solution of silver. Because of the small yields of aldehyde and acid, it was not possible to investigate them in detail. Our attention was drawn to the product of ozonolysis which did not distil with steam.

Investigation of the product of ozonation not volatile with steam

0.0988 g substance. 0.2526 g CO₂, 0.0950 g H₂O.
0.0962 g substance. 0.2460 g CO₂, 0.0922 g H₂O.
Found %: C 69.72, 69.74; H 10.69, 10.62.
C₁₉H₃₄O₄. Computed %: C 69.94; H 10.43.
C₁₉H₃₆O₄. Computed %: C 69.51; H 10.98.
0.0358 g substance. 0.4214 g camphor: Δ t 10° (Rast).
0.0348 g substance. 0.3272 g camphor: Δ t 13°.
Found: M 324, 327.
C₁₉H₃₄O₄. Computed. M 326.
C₁₉H₃₆O₄. Computed: M 328
0.1062 g substance: consumed 0.01762 g KOH (titration)
0.1064 g substance: consumed 0.01828 g KOH.
Found. M 326.7, 326.5.
0.0738 g substance: 7.2 ml CH₄ (0°, 760 mm).
0.0750 g substance. 7.4 ml CH₄ (0°, 760 mm).
0.0796 g substance: 7.9 ml CH₄ (0°, 760 mm).
Found OH: 1.43, 1.45, 1.45.
C₁₉H₃₄O₄. Computed OH: 1.
C₁₉H₃₆O₄. Computed OH: 2.

The preparation of semicarbazones

0.72 g of semicarbazide hydrochloride and 0.64 g of potassium acetate were dissolved in a small amount of water, and 20 ml of methyl alcohol was added to the mixture. After the precipitated potassium chloride had been removed, 0.5 g of the ozonation product non-volatile with steam was added to the filtrate. The precipitated semicarbazone was separated, washed with water, and then with alcohol, and dried. M.p. 229-229.5°. From the filtrate after removal of the semicarbazone precipitate, a yellow oil was obtained. It was dissolved in ether, washed with water, and dried. After the ether had been removed, the oil, like the precipitate, was subjected to analysis.

Determination of nitrogen (Kjeldahl), in crystalline semicarbazone.

0.0140 g substance: consumed 0.00931 g H₂SO₄.
0.0220 g substance: consumed 0.01470 g H₂SO₄.
Found %: N 19.00, 19.11.

C₂₁H₄₀C₄N₆. Computed %: N 19.09.

Extraction with ether made possible the separation of the small amount of aldehyde.

Determination of nitrogen (Kjeldahl) in liquid semicarbazone.

0.0602 g substance: consumed 0.02278 g H_2SO_4 .

0.0584 g substance: consumed 0.02205 g H_2SO_4 .

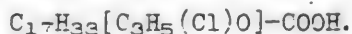
Found %: N 10.83, 10.80.

$C_{20}H_{39}O_4N_3$. Computed %: N 10.91.

SUMMARY

1. The action of formalin on oleic acid in the presence of H_2SO_4 gave a condensation product of oleic acid with formaldehyde with the composition $C_{21}H_{40}O_4$.

2. The ethyl ester of the condensation product had the composition $C_{17}H_{33}[C_3H_5(OH)O]-COOC_2H_5$, and the chloro derivative had the composition

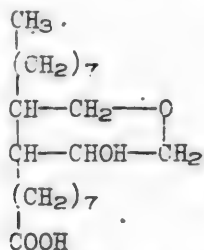


3. Oxidation of the original substance $C_{21}H_{40}O_4$ with chromic anhydride gave the ketoacid $C_{17}H_{33}[C_2H_4(CO)O]-COOH$. The ketoacid gave an oxime, a semicarbazone, and an ethyl ester.

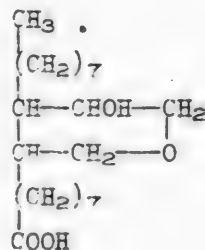
4. Dehydration of the original substance led to the unsaturated ketoacid $C_{17}H_{33}[CH_3(CH=C)O]-COOH$.

5. Ozonation of the unsaturated acid $C_{21}H_{38}O_3$ gave the ketoaldo acid $C_{19}H_{34}O_4$ and the ketohydroxy acid $C_{19}H_{36}O_4$.

6. Analysis of all the substances obtained, as well as of the product of ozonization of the unsaturated acid, enabled us to arrive at the conclusion that the condensation product $C_{21}H_{40}O_4$ was a heterocyclic acid and had one of the following formulas:



or



7. A mechanism of condensation is given.

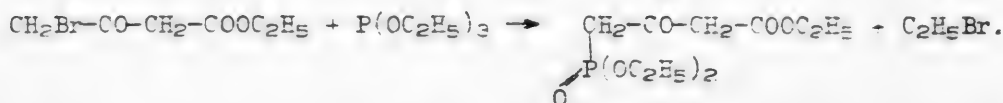
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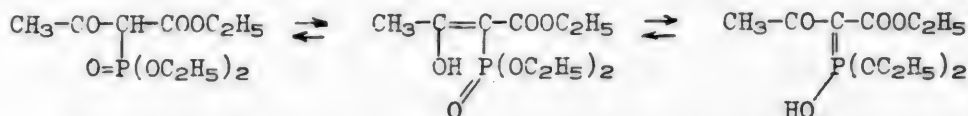
The action of α -halogen ketones on the esters of phosphorous acid and on sodium diethyl phosphite has been studied by a number of investigators. Thus, P. Nylen [1] attempted to carry out the reaction of sodium diethyl phosphite with *o*-bromoacetophenone and chloroacetophenone, but the reaction took place abnormally and Nylen could not isolate the corresponding diethylphosphonoketones. A.E. Arbuzov and A.I. Razumov [2] were able to synthesize diethylphosphonacetophenone by the action of bromoacetophenone on triethyl phosphite, as well as on sodium diethyl phosphite, and to study some of its properties. A.I. Razumov and N. Petrov [3] synthesized the diethyl ether of phosphonacetone by the action of triethyl phosphite on bromoacetone in two forms with different boiling points, of which only one gave a semicarbazone. A.E. Arbuzov and A.I. Razumov [2] and A.I. Razumov and N. Petrov [3] showed that the ethers of phosphonacetophenone and of phosphonacetone reacted with sodium. When the reaction product with sodium was treated with an alkyl halide, further reaction took place. However, it was impossible to isolate the reaction product. This sort of behavior of the ethers of the α -phosphone ketones differs from the behavior of the esters of α -phosphone carboxylic acids, where after the substitution of the hydrogen in the α -position by sodium and the action of alkyl halide, normal reaction products are obtained [4]. The abnormal behavior of the ethers of phosphonacetone and phosphonacetophenone led us to carry out further syntheses of compounds which contained the carbonyl group in the β -position to the phosphone group, and to study some of their properties.

$$\text{CH}_3\text{-CO-CHBr-COOC}_2\text{H}_5 + \text{P(OC}_2\text{H}_5)_3 \rightarrow \text{CH}_3\text{-CO}-\underset{\begin{array}{c} \text{O} \\ || \\ \text{P(OC}_2\text{H}_5)_2 \end{array}}{\text{CH}}\text{-COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{Br}$$


1528-

- I. 138-142° (3 mm), n_D^{20} 1.4445, d_4^{20} 1.1409 (50%);
 II. 142-144° (3 mm); n_D^{20} 1.4443, d_4^{20} 1.1559 (15%).

In accordance with the analysis, both fractions corresponded accurately to diethylphosphonacetoacetic ester. The explanation of this extensive boiling range might lie in the possible existence of α -phosphonacetoacetic ester in a keto and an enol (or several enol) forms.



Titration of fractions I and II with bromine (method of K. Meyer [5]) showed however that there was negligible addition of bromine to both fractions, corresponding to 0.22% enol for the 1st fraction, and 0.21% for fraction II.

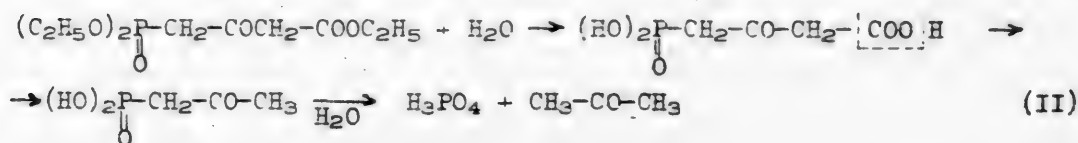
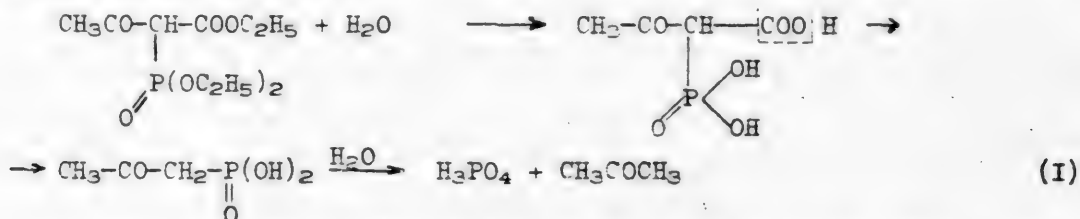
A similar picture was observed in the case of the reaction of triethyl phosphite with γ -bromoacetoacetic ester. This reaction gave a product with the extensive boiling range of 135-158° (2 mm) in a yield 60% of theory. Distillation of the product with boiling range 135-158° (2 mm) into fractions showed that all of them corresponded on analysis to diethylphosphonacetoacetic ester, and that all had very little and almost identical unsaturation:

- I. 135-145° (2 mm), n_D^{20} 1.4400, d_4^{20} 1.1486 (13%) 1.05% enol.
 II. 145-150° (2 mm); n_D^{20} 1.4400, d_4^{20} 1.1517 (30%) 0.88% enol.
 III. 150-156° (2 mm); n_D^{20} 1.4451, d_4^{20} 1.1737 (16%) 1.81% enol.

Another explanation of the extensive boiling range of diethylphosphonacetoacetic ester might be the possibility of transformation of the α -bromoacetoacetic ester into the γ -bromoacetoacetic ester, which might have taken place under the influence of hydrogen bromide [6].

There are indications [7] in the literature that α -iodoacetoacetic ester is not transformed into γ -iodoacetoacetic ester under the influence of hydrogen iodide in the presence of hydrogen peroxide, and this induced us to set up an experiment on the reaction of α -iodoacetoacetic ester with triethyl phosphite. However, in this case too the diethyl phosphonacetoacetic ester obtained had the same extended boiling range.

The action of phenylhydrazine and semicarbazide on the fractions obtained in the experiments with α -bromoacetoacetic ester and γ -bromoacetoacetic ester did not permit the isolation of crystalline derivatives. Saponification of the diethylphosphonacetoacetic ester obtained both in the experiments with α -bromoacetoacetic ester and with γ -bromoacetoacetic ester, using hydrochloric acid at 120-130°, did not result in the expected phosphonacetone. In both cases, saponification led to the formation of acetone and phosphoric acid, and took place, apparently, in accordance with the mechanism:



Thus, these examples show that the phosphone group behaves like the carboxyl group, and the β -ketophosphinic acids like the β -keto carboxylic acids, being unstable, and splitting off the elements of phosphoric acid upon hydrolysis.

The examples given once more emphasized the similarity between the phosphone group and the carboxyl group, noted by A.E. Arbuzov [8].

Both in the case of the phosphonacetoacetic ester obtained from α -bromoacetoacetic ester and that from γ -bromoacetoacetic ester, the action of sodium and then of alkyl halide did not result in the isolation of products in which the hydrogen of the phosphonacetoacetic ester was substituted by alkyl.

The saponification of the ester of phosphonacetoacetic acid with hydrochloric acid probably results in the formation of β -ketophosphinic acids as intermediate products, and these then split up into acetone and phosphoric acid. In order to confirm the possibility of this sort of cleavage of β -ketophosphinic acids, we studied the action of triethyl phosphite and sodium diethyl phosphite on 2-chloro and 2-bromo cyclohexanone.

The action of triethyl phosphite on 2-chlorocyclohexanone gave the diethyl ester of cyclohexanon-2-phosphinic acid in a yield 54.5% of the theoretical.



The ester had b.p. 160-163° (17 mm); n_D^{20} 1.4510, and d_4^{20} 1.1234.

Upon saponification with dilute hydrochloric acid by heating in a sealed tube at 160°, the ester was split up into cyclohexanone and phosphoric acid. The cyclohexanone was identified by the formation of its semicarbazone with m.p. 155-156°; the phosphoric acid by the formation of phenylhydrazine phosphate, with m.p. 154-155°.

This same product, the diethyl ester of cyclohexanon-2-phosphoric acid, was obtained by us by the action of sodium diethyl phosphite both on 2-chloro- and on 2-bromocyclohexanone.

For a comparison of the behavior of the β -ketophosphinic esters with that of the δ -ketophosphinic esters upon saponification, we carried out experiments on the action of triethyl phosphite and sodium diethyl phosphite on 5-bromopentanone-2 in order to obtain representatives of the δ -ketophosphinic esters. We were unable to synthesize the ethyl ester of γ -acetopropylphosphinic acid by the action of triethyl phosphite on methyl- γ -bromopropyl ketone. As the chief product of the reaction we obtained diethylphosphorous acid. The reaction was carried out at 135-145°, and was accompanied by the separation of ethyl bromide. The formation of diethylphosphorous acid under these conditions could be explained by the splitting off of hydrogen bromide from the bromoketone. The hydrogen bromide and triethyl phosphite gave ethyl bromide and diethylphosphorous acid:



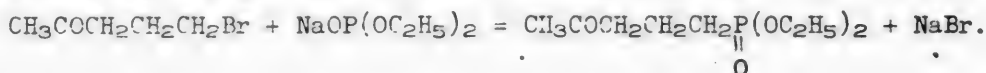
In fact, a separate experiment showed that methyl- γ -bromopropyl ketone, upon heating to 135-145°, quickly darkened, and at 160-165° evolved hydrogen bromide. The presence of the triethyl phosphite, which was ready to react with the hydrogen bromide, in all probability facilitated the splitting off of the latter.

The action of methyl- γ -bromopropyl ketone on sodium diethyl phosphite gave the expected ethyl ester of γ -acetopropylphosphinic acid, $CH_3-CO-(CH_2)_2CH_2PO(OC_2H_5)_2$, in a yield of 62.4% of theory, in the form of a

colorless liquid with the following constants: b.p. 115-117° (9 mm); n_D^{20} 1.4422; d_4^{20} 1.1155; d_4^{20} 1.0865.

When the ester was saponified with hydrochloric acid at 100-110°, a viscous liquid was obtained, from which the lead salt was formed. This corresponded, as far as analysis went, to the expected γ -acetopropylphosphinic acid.

Thus, like the δ -ketocarboxylic acid, the δ -ketophosphinic acids are stable in the free form. The reaction between methyl- γ -bromopropyl ketone and sodium diethyl phosphite may be expressed by the following equation:



EXPERIMENTAL

The action of α -bromoacetoacetic ester on triethyl phosphite

(B. P. Lugovkin)

To 43.2 g of α -bromoacetoacetic ester (b.p. 93-98° at 11 mm, n_D^{20} 1.4608; d_4^{20} 1.4232 [9]), which was placed in a distilling flask and heated to 100°, there was added, drop by drop, 37.1 g of triethyl phosphite. The evolution of ethyl bromide took place. The temperature in the flask was 125-133°. 17 g of ethyl bromide with b.p. 36-38° were given off (theory 22.5 g). The reaction product, after two distillations, at 3 mm, gave the following fractions:

1. 138-142° (3 mm), n_D^{20} 1.4445, d_4^{20} 1.1573; d_4^{20} 1.1409. Weight 27.5 g.
2. 142-144° (3 mm); n_D^{20} 1.4448, d_4^{20} 1.1727; d_4^{20} 1.1559. Weight 8.3 g.

Titration (K. Meyer) gave unsaturation for (1) corresponding to 0.22% enol; for (2) 0.21% enol.

The fractions were colorless liquids, without odor, and insoluble in water.

Analysis of the fraction 138-142° (3 mm):

0.1286 g substance. consumed 23.71 ml NaOH (titer 0.02282).

Found %: P 11.64.

$\text{C}_{10}\text{H}_{19}\text{O}_6\text{P}$. Computed %: P 11.65.

Analysis of the fraction 142-144° (3 mm):

0.1218 g substance. consumed 23.09 ml NaOH.

0.1174 g substance. consumed 22.01 ml NaOH.

Found %: 11.98, 11.85.

Saponification. 4.8 g of the 138-142° fraction (3 mm) was heated with 25 ml of hydrochloric acid in a sealed tube at 120-130° for 10 hours. When the tube was opened, the evolution of ethyl chloride and CO_2 (BaCO_3) was observed. After the water had been driven off, acetone was detected in the distillate in the form of indigo by Baeyer's reaction [10]. The residue, after the removal of the water and HCl (1.9 g) was a viscous liquid. Phenylhydrazine (2.1 g) was added to it. The reaction product quickly hardened. After recrystallization from alcohol, 2.8 g of phenylhydrazine phosphate was obtained, with m.p. 153-154°. A mixed test with phenylhydrazine phosphate gave no change of melting point [11].

The reaction for the carbonyl group. To 1.95 g of the substance, 0.83 g of phenylhydrazine was added, and the mixture was heated on the water bath for 2 hours. A dark-colored oil was obtained. This did not crystallize after standing for several months.

To 1.96 g of the substance, 0.82 g of semicarbazide hydrochloride in solution in alcohol and 1 g of sodium acetate in 30 ml of methyl alcohol were added.

A crystalline semicarbazone did not precipitate even after long standing.

The action of sodium and propyl bromide on the diethyl ether of
 α -phosphonacetoacetic ester

To a solution of sodium propylate, prepared from 1.3 g of sodium and 34 ml of propyl alcohol, 15 g of α -phosphonacetoacetic ester was added. A slight evolution of heat took place. Upon the addition of 10 g of propyl bromide, another mild evolution of heat occurred. No sodium bromide precipitated, even after heating with a reflux condenser for an hour. After removal of the alcohol, the residue was fractionally distilled to give 4.9 g of a fraction with b.p. 78-80° (2 mm); n_D^{20} 1.4310; d_4^{20} 1.0134. Analysis of this fraction gave the following results:

Found %: P 6.53, 6.47; C 54.30; H 9.06.
 $C_{13}H_{25}O_6P$. Computed %: P 10.06; C 50.65; H 8.11.

The action of α -iodoacetoacetic ester on sodium diethyl phosphite

(B. P. Lugovkin)

To 32.6 g of α -iodoacetoacetic ester [7], dissolved in 50 ml of dry ether, an ether solution of sodium diethyl phosphite was added; this was prepared from 19 g of diethyl phosphoric acid and 3 g of sodium in 250 ml of dry ether. A precipitate of sodium iodide formed. After the ether had been driven off, the reaction product was fractionated in vacuum several times. Two fractions were obtained:

I. B.p. 143-149° (3.5 mm); n_D^{20} 1.4370; d_4^{20} 1.1407 in the form of a colorless liquid soluble in water (in contrast to the product obtained from α -bromoacetoacetic ester, which was insoluble in water). It gave a very weak color with an aqueous solution of $FeCl_3$.

Found %: P 13.0
 $C_{10}H_{19}O_6P$. Computed %: P 11.65.

II. B.p. 149-155° (3.5 mm); n_D^{20} 1.4370; d_4^{20} 1.1553; a liquid soluble in water. It gave no color with an aqueous solution of $FeCl_3$. Found %: P. 14.85, 14.71. Total weight of fractions I and II 5.4 g.

The action of triethyl phosphite on γ -bromoacetoacetic ester

(B. P. Lugovkin)

To 58.2 g of γ -bromoacetoacetic ester (b.p. 107-110° (10 mm); n_D^{20} 1.4828; d_4^{20} 1.5263) [9], which was placed in a distilling flask and heated to 100°, there was added, drop by drop, 50.2 g of triethyl phosphite. The ethyl bromide distilled off at a temperature from 130-135°. 23.7 g of the ethyl bromide was obtained (theory 30.3 g). After two consecutive distillations, the reaction product gave the following fractions.

I. B.p. 135-145° (2 mm); n_D^{20} 1.4400; d_4^{20} 1.1486. Weight 9.6 g. Titration (K. Meyer) gave an unsaturation of 1.05% calculated as enol.

II. B.p. 145-150° (2 mm); n_D^{20} 1.4400; d_4^{20} 1.1517. Weight 22.5 g. Unsaturation calculated as enol 0.86%.

III. B.p. 150-158° (2 mm); n_D^{20} 1.4451; d_4^{20} 1.1737. Weight 11.7 g. Unsaturation calculated as enol 1.81%.

All the fractions were colorless liquids, soluble in water.

Analysis of the 135-145° (2 mm) fraction:

0.1392 g substance: 25.42 ml NaOH ($T = 0.02282$).
Found %: P 11.54.
 $C_{10}H_{19}O_6P$. Computed %: P 11.65.

0.1824 g substance: 0.2972 g CO₂; 0.1183 g H₂O.
Found %: C 44.40; H 7.18.
C₁₀H₁₉O₆P. Computed %: C 45.11; H 7.14.

Analysis of the 145-150° (2 mm) fraction:

0.1322 g substance: 24.81 ml NaOH.
Found %: P 11.86.
0.1572 g substance: 0.2549 g CO₂; 0.1003 g H₂O.
0.2306 g substance: 0.3780 g CO₂; 0.1625 g H₂O.
Found %: C 44.21, 44.70; H 7.06, 7.80.

Analysis of the 150-158° (2 mm) fraction:

0.1698 g substance: 30.51 ml NaOH.
Found %: P 11.36.
0.1673 g substance: 0.2758 g CO₂; 0.1076 g H₂O.
Found %: C 44.94; H 7.11.

Saponification. 6.2 g of the fraction with b.p. 150-158° (2 mm) and 40 ml of hydrochloric acid (19%) were heated for 8 hours at 120-130°. When the tube was opened, CO₂ (BaCO₃) and ethyl chloride were given off. After the aqueous solution had been driven off, acetone was detected in the distillate by Baeyer's test. The residue, after the distillation of the water and removal of the HCl by repeated evaporation, was a viscous liquid (3.15 g). The action of phenylhydrazine upon it gave 2.6 g of phenylhydrazine phosphate with m.p. 154° (in a mixed test).

Reaction for the carbonyl group. The action of phenylhydrazine on the fractions with b.p. 145-150° and 150-158° did not give crystalline phenylhydrazones. The action of semicarbazide on the fraction 135-145° did not give a crystalline semicarbazone.

The action of sodium and benzyl chloride. The 145-150° fraction (15.3 g) was added drop by drop to 1.37 g of sodium in 60 ml of benzene. An energetic reaction took place, with the evolution of hydrogen. Then 7.4 g of benzyl chloride was added, and the entire mixture was heated at the boiling point of benzene for 3.5 hours. No sodium chloride precipitated. After the benzene had been driven off along with the unreacted benzyl chloride in vacuum, a viscous liquid was obtained, which did not distil in vacuum. Upon saponification with dilute hydrochloric acid by boiling for 10 hours, ethyl chloride and CO₂ were given off. After concentration, the residue was extracted with absolute alcohol. After the HCl had been driven off, the action of phenylhydrazine on the alcoholic extract gave 9 g of phenylhydrazine phosphate with m.p. 154°. The residue from the treatment with alcohol gave 2 g of sodium chloride (theory 2.8 g).

The action of triethyl phosphite on 2-chlorocyclohexanone

(N. P. Rogonostseva)

The 2-chlorocyclohexanone had b.p. 86° (12 mm) and m.p. 18-20° [12].

The 2-chlorocyclohexanone (10 g) was melted and 13 g of triethyl phosphite was added to it. Upon heating to 60°, the evolution of ethyl chloride began. The heating was continued for 2 hours at a temperature of 100-120°. The reaction product was fractionated in vacuum. The fractions obtained were: 80-160° (17 mm), 3.8 g; and 160-163° (17 mm), 13.6 g (54.4% of theory).

The 160-163° (17 mm) fraction had n_D^{20} 1.4510; d_4^{20} 1.1234. Analysis for phosphorus content required very lengthy oxidation of the substance (104 hours with three additions of nitric acid). Less lengthy heating resulted in low values of the phosphorus content.

0.0704 g substance: 19.24 ml NaOH ($T = 0.01848$).

0.0620 g substance: 16.73 ml NaOH ($T = 0.01848$).

Found % P 13.98, 13.80.

$C_{10}H_{18}O_4P$. Computed % P 14.16.

Saponification. 9.3 g of the substance and 25 ml of 20% hydrochloric acid were heated for 10 hours at 160° in a sealed tube. The insoluble product separated from the aqueous layer in the form of an oil. The aqueous layer was extracted with ether. Half of the oily layer was distilled in vacuum. A $60-70^\circ$ fraction (30 mm) was separated, and a small amount of a fraction from 70 to 170° (24 mm) (with decomposition).

The $60-70^\circ$ fraction consisted of cyclohexanone. Upon treatment with semicarbazide, it gave the semicarbazone of cyclohexanone, with m.p. $155-156^\circ$. A semicarbazone with m.p. $155-156^\circ$ was obtained from the oily layer from the saponification without a preliminary distillation in vacuum. The aqueous portion from the saponification was evaporated several times with water in order to remove the hydrochloric acid completely. The viscous liquid which was left after the evaporation was treated with phenylhydrazine. It gave phenylhydrazine phosphate, with m.p. $154-155^\circ$ (mixed test). From 0.5 g of the residue, 0.25 g of phenylhydrazine phosphate was obtained.

The action of 2-chlorocyclohexanone on sodium diethyl phosphite

(N. P. Bogonostseva)

To an ether solution of 2-chlorocyclohexanone (23 g) an ether solution of sodium diethyl phosphite was added (from 24.1 g of diethyl phosphorous acid and 4.8 g of sodium). There was an evolution of heat. The ether boiled, and a precipitate of sodium chloride formed. After the precipitate had been removed, the ether was driven off. Upon fractionation, the residue gave the following fractions: I - $110-149^\circ$ (11 mm); II - $149-151^\circ$ (11 mm). Upon further distillation, the second fraction gave a fraction with b.p. $148-150^\circ$ (11.5 mm); n_D^{20} 1.4518; d_4^{20} 1.1380, weight 10 g, a fraction with b.p. $151.5-155^\circ$ (11.5 mm); n_D^{20} 1.4569; d_4^{20} 1.1400, weight 16.3 g (42.9% of theory). The NaCl obtained was washed with ether, dissolved in water, and evaporated. It amounted to 9.9 g, or 97.5% of theory.

The action of 2-bromocyclohexanone on sodium diethyl phosphite.

(N. P. Bogonostseva)

23 g of bromocyclohexanone (b.p. $94-109^\circ$ at 17 mm [13]) was dissolved in ether and to the solution there was added an ether solution of sodium diethyl phosphite prepared from 2.4 g of sodium and 18 g of diethyl phosphorous acid. The reaction took place with a vigorous evolution of heat and boiling of the ether. The usual treatment, and the distillation of the residue in vacuum, after the ether had been driven off, gave 9 g of a fraction (31.6% of theory) with b.p. $148-149^\circ$ (11.5 mm), n_D^{20} 1.4578; d_4^{20} 1.1270. The NaBr was washed with ether, dissolved in water, and the aqueous layer evaporated to dryness. The residue was dried. Yield of NaBr 11.1 g, or 82% of theory.

The action of γ -bromopropylmethyl ketone on triethyl phosphite

(B. P. Lugovkin)

To 34 g of triethyl phosphite (theory 30.1 g) which was heated to $135-145^\circ$, 30 g of the bromoketone (with b.p. $71-72^\circ$ at 9 mm, n_D^{20} 1.4671 [14]) was added over a period of 2 hours. The evolution of ethyl bromide took place. The reacting liquid took on a dark brown color. The reaction was completed by heating at $160-170^\circ$ until there was no more evolution of ethyl bromide. The ethyl bromide given off amounted to 13.5 g. When the reaction liquid was distilled in vacuum, it gave 16.5 g of a fraction with b.p. $58-62^\circ$ (8 mm); n_D^{20} 1.4090. Upon repeating the

distillation, 14.8 g of a fraction with b.p. 63-64° (7 mm); n_D^{20} 1.4080; d_4^{20} 1.0916 was obtained. From the data and the analysis, this corresponded to diethyl phosphorous acid.

Found %: P 21.82.

$C_4H_{11}O_3P$. Computed %: P 22.46.

The action of γ -bromopropylmethyl ketone on sodium diethyl phosphite

(B. P. Lugovkin)

To 37.7 g of the bromoketone, diluted with 50 ml of dry ether, there was added drop by drop, with careful stirring, an ether solution of sodium diethyl phosphite, prepared from 33 g (theory 30.9 g) of diethyl phosphorous acid and 5.2 g of sodium in 500 ml of dry ether. Heat was evolved and sodium bromide precipitated. The ether solution was decanted from the precipitate of sodium bromide. After washing with acetone, the sodium bromide weighed 22.0 g, or 89.4% of theory. After the ether had been driven off, the reaction product was distilled in vacuum to give 31.4 g of a fraction with b.p. 108-112° (8 mm); n_D^{20} 1.4419, or 62.5% of theory. After another distillation, the γ -acetopropylphosphinic ester (27.4 g) had the following constants: b.p. 115-117° (9 mm); n_D^{20} 1.4422; d_4^{20} 1.0865.

0.0796 g substance. consumed 18.4 ml NaOH ($T = 0.02126$).

0.0676 g substance. consumed 17.2 ml NaOH ($T = 0.02126$).

0.1710 g substance. 0.3052 g CO_2 ; 0.1346 g H_2O .

Found %: P 13.61, 13.74.

Found %: C 48.57; H 8.74.

$C_9H_{19}O_4P$. Computed %: P 13.95; C 48.64; H 8.55.

The phenylhydrazone and the 2,4-dinitrophenylhydrazone of the γ -acetopropyl phosphinic ester could not be obtained.

Saponification. 3.4 g of the substance was heated with 14 ml of dilute hydrochloric acid (1:1) in a sealed tube at 100-110° for 9 hours. After repeated evaporation on the water bath with the addition of water, 2.5 g of a viscous liquid with a light yellow color was obtained. This could not be crystallized. The action of barium carbonate upon an aqueous solution of this substance gave a barium salt soluble in water. The salt could not be obtained in an analytically pure form. The action of silver nitrate on the ammonium salt of γ -acetopropyl phosphinic acid took place with reduction to metallic silver. The action of a solution of lead acetate on the ammonium salt in aqueous solution gave a lead salt with a pale rose color.

0.3126 g substance. 0.2598 g $PbSO_4$.

Found %: Pb 0.1776

$C_5H_9PO_4Pb$. Computed %: Pb 0.1744

SUMMARY

1. The action of triethyl phosphite on α -bromoacetoacetic and γ -bromoacetoacetic esters gave ethers of the corresponding phosphonacetoacetic esters.

The products obtained had extended boiling ranges. However, analysis of the separate fractions showed that in composition they all corresponded to the ethyl ether of phosphonacetoacetic ester.

2. Upon saponification with hydrochloric acid, the compounds obtained underwent cleavage to give acetone and phosphoric acid.

3. The action of triethyl phosphite and sodium diethyl phosphite on chloro- and bromo-cyclohexanone gave the ethyl ester of cyclohexanon-2-phosphinic acid, which upon saponification with hydrochloric acid was split into cyclohexanone and phosphoric acid.

These examples have shown that the phosphone group behaves like the carbonyl group in β -ketocarboxylic acids.

4. The action of sodium diethyl phosphite on methyl- γ -bromopropyl ketone gave the ethyl ester of γ -acetopropylphosphinic acid.

Saponification of the ester of γ -acetopropylphosphinic acid with hydrochloric acid did not result in the cleavage of γ -acetopropylphosphinic acid.

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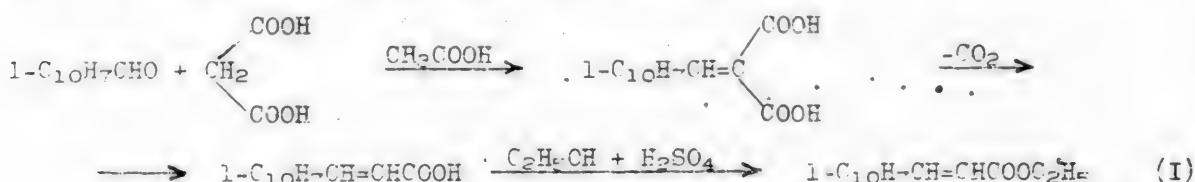
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THE QUESTION OF THE METHODS OF PREPARATION OF β -(NAPHTHYL-1)-ACRYLIC ACID AND ITS ETHYL ESTER

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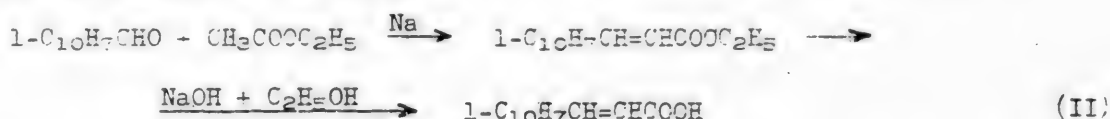
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Among the different methods for the preparation of β -(naphthyl-1)-acrylic acid; up to the present time the method of condensation of α -naphthaldehyde with malonic acid, with the subsequent splitting off of CO_2 from the α -naphthylmalonic acid [1] formed (I) may be considered the most convenient:



The method of Claisen, the condensation of aromatic aldehydes with ethyl acetate in the presence of sodium, so successfully applied to the preparation of the ethyl ester of cinnamic acid [2], has been utilized in the naphthalene series only for the preparation of (4-methoxynaphthyl-1)-acrylic acid [3].

We carried out the condensation of 1-naphthaldehyde with ethyl acetate, and observed that this reaction is especially useful for the preparation of β -(naphthyl-1)-acrylic acid (II):



As for the ethyl ester of β -(naphthyl-1)-acrylic acid, in addition to the indisputable advantage of the Claisen reaction there is also a decrease in the number of steps in comparison with mechanism (I) (one instead of three), but the yield of chemically pure ester with m.p. $37\text{-}38^\circ$ is small, so that its isolation in crystalline form requires careful purification of the condensation product (two distillations in vacuum plus a subsequent recrystallization), and this is attended with considerable loss of material.

If we make it our objective to obtain β -(naphthyl-1)-acrylic acid according to mechanism (II), then it is sufficient to limit ourselves to a single distillation of the condensation product in vacuum. The distilled material (yield 70-72%)

A detailed review of the methods of preparation of β -(naphthyl-1)-acrylic acid is given in the candidates' dissertations of A. S. Elina and K. V. Levshina.

consists chiefly of the ethyl ester of β -(naphthyl-1)-acrylic acid. The ester of this quality is entirely suitable for synthetic purposes; and its saponification gives β -(naphthyl-1)-acrylic acid in a yield of 60-62%, calculated on the basis of the 1-naphthaldehyde.

EXPERIMENTAL

β -(Naphthyl-1)-acrylic acid

a) The condensation of 1-naphthoic aldehyde with ethyl acetate. In a three-necked flask, fitted with a mechanical stirrer, a thermometer, and a dropping funnel, there were placed 4 g of finely divided sodium and 80 ml of ethyl acetate. The contents of the flask were quickly cooled to 0°, 1 ml of absolute ethyl alcohol was added, and then, from the dropping funnel, there were added gradually, with constant stirring, 20 g of 1-naphthaldehyde. The reaction was carried out at 0-5°. After the addition of the 1-naphthoic aldehyde, the reaction mixture was stirred at the same temperature for an additional three hours. Then 20 ml of glacial acetic acid was carefully added, and the crystalline precipitate that formed as a result was dissolved by the addition of 60 ml of water. The contents of the flask were transferred into a separatory funnel, and a small additional amount of ethyl acetate was added. The mixture was shaken and the upper layer removed. The lower layer was extracted several times with ethyl acetate. All the ethyl acetate solutions were combined, washed with a 10% solution of soda,* then with water, dried over sodium sulfate, and the ethyl acetate driven off. The oily brown liquid which remained, 28 g in amount**, was distilled in vacuum. The fraction collected boiled from 170-197° at 10-12 mm (most of it boiled from 180-197°). 21 g was obtained (72%, based on the 1-naphthaldehyde).

b) Saponification of the ethyl ester of β -(naphthyl-1)-acrylic acid. 21 g of the ethyl ester of β -(naphthyl-1)-acrylic acid, which had been distilled in vacuum once, was dissolved with heating in absolute ethyl alcohol, and a solution of 4.2 g of caustic soda in 110 ml of absolute alcohol was added. The mixture was allowed to stand overnight; at the end of this period, a voluminous precipitate of the sodium salt of β -(naphthyl-1)-acrylic acid formed. This was filtered off, and the alcohol driven from the filtrate almost to dryness. The residue and the sodium salt previously filtered were united, dissolved in water, filtered, and the filtrate acidified with 10% hydrochloric acid. The β -(naphthyl-1)-acrylic acid which separated out was filtered with suction and washed on the filter with toluene. An almost white powder was obtained with m.p. 203-207° (14.6 g). Taking into account the 0.9 g obtained from the soda wash-solution, the total yield of β -(naphthyl-1)-acrylic acid equaled 15.5 g, which amounted to 83%, calculated on the basis of the ethyl ester, and 60%, calculated on the basis of the 1-naphthaldehyde.

If β -(naphthyl-1)-acrylic acid of this quality is subjected to recrystallization from methyl or ethyl alcohol, colorless needles with m.p. 208-210° are obtained. The yield ranges from 43 to 47%, based on the 1-naphthaldehyde.

The ethyl ester of β -(naphthyl-1)-acrylic acid

The condensation of 1-naphthaldehyde (20 g) with ethyl acetate (80 ml) in the presence of metallic sodium (4 g), and the further treatment of the reaction

* The solution of soda used for washing was acidified with hydrochloric acid to give a small amount (1.05g) of β -(naphthyl-1)-acrylic acid with m.p. 195-198° after washing with toluene, 0.9 g of the acid was obtained, with m. p. 203-207° (caking began at 200°).

** Experiments on the saponification of the undistilled reaction product did not give better yields of β -(naphthyl-1)-acrylic acid, as the latter was obtained in very impure form, and its purification resulted in a considerable lowering of the yield.

product up to distillation in vacuum, were carried out in the same way as described in the preceding experiment. After the first distillation in vacuum, the fraction which boiled from 170-195° at 10-12 mm was distilled again. The substance distilled at 190-197° at 10-12 mm, and upon standing, almost completely crystallized in the receiver. After recrystallization from ethyl alcohol, 10 g of the ethyl ester of β -(naphthyl)-1-acrylic acid was obtained (33%, based on the 1-naphthaldehyde), with m.p. 37-38.5°.

SUMMARY

A description is given of methods previously not customarily used for the preparation of the ethyl ester of β -(naphthyl-1)-acrylic acid by the condensation of 1-naphthaldehyde with ethyl acetate and for the preparation of β -(naphthyl-1)-acrylic acid by saponification of the ethyl ester thus obtained.

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(5 NITRONAPHTHYL-1) PROPIOLIC ACID AND ITS TRANSFORMATIONS

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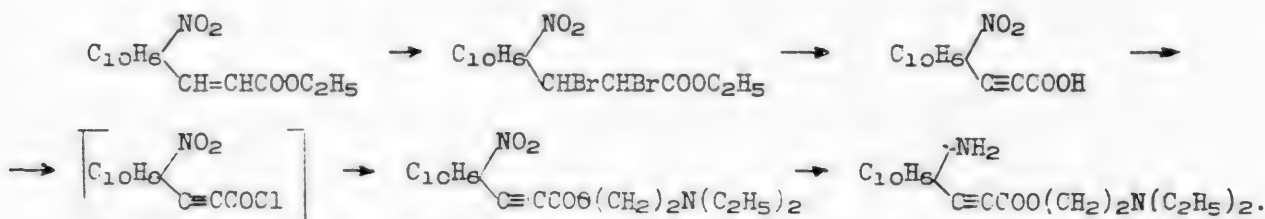
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In an investigation of the relationship between the anaesthetic action of compounds of the type of novocaine [$H_2NArCOO(CH_2)_nNR_2$] and their structure, it was found that the conjugation of the double bond of the carbonyl group with the double bond of the benzene ring was one of the most important factors for the appearance of anaesthetic properties in the esters. The ethylene bond situated between these double bonds did not decrease, but sometimes even increased, the anaesthetic action. Upon substituting this ethylene bond with a saturated bond, or an unsaturated triple bond, the anaesthetic action of the esters disappeared. Similar phenomena were also observed in the naphthalene series during the investigation of alkamino esters of aminonaphthyl acrylic and aminonaphthyl propionic acids [1].

The anaesthetic action of alkamino esters of naphthyl propiolic acids has not yet been tested. It appeared to us of interest to get a more precise picture, from this point of view, of the role of the triple bond in compounds of a similar type and in the naphthalene series.

In view of the fact that (5-nitronaphthyl-1)-acrylic acid was accessible to us, we chose it as the starting material for the preparation of alkamino esters of (5-aminonaphthyl-1)-propionic acid.

The synthesis of this compound is shown by the following equations:



Difficulties were encountered in the first two steps: 1) in the addition of bromine to the ethylene bond, and 2) in the preparation of (5-nitronaphthyl-1)-propionic acid. The experiments on the addition of bromine gave positive results only when the ethyl ester of 5-(nitronaphthyl-1)-acrylic acid was brominated at room temperature. It was impossible to introduce 2 atoms of bromine into the molecule of the free (5-nitronaphthyl-1)-acrylic acid, despite numerous attempts made under various conditions. The splitting off of the elements of hydrogen bromide from the ethyl ester of (5-nitronaphthyl)-1 dibromopropionic acid was accomplished by means of an alcoholic solution of caustic potash, which at the same time saponified the ester group.

The (5-nitronaphthyl-1)-propionic acid is an unstable compound. Upon heating, or even upon storage, the splitting off of carbon dioxide takes place, and

there is the formation of (5-nitronaphthyl-1)-acetylene. This property of the acid considerably complicates its isolation, its purification, and the determination of its melting point. The fact that the change of (5-nitronaphthyl-1)-propionic acid takes place in precisely this direction is confirmed by the ease of formation of (5-nitronaphthyl-1)-acetylene when the acid is heated with pyridine, and by a comparison of the properties of (5-nitronaphthyl-1)-acetylene with the properties of the cleavage products of (5-nitronaphthyl-1)-propionic acid.

The ethyl ester of (5-nitronaphthyl-1)-propionic acid, obtained by the esterification of the acid, is a very stable compound, and does not have any of the cited properties of the acid.

We were also interested in the properties of (5-aminonaphthyl-1)-propionic acid. Therefore the nitro group in the ethyl ester of (5-nitronaphthyl-1)-propionic acid was reduced. However, we did not succeed in obtaining the ester of the corresponding amino acid in crystalline form, but by the treatment with acetic anhydride of the oily substance obtained after reduction of the nitro group we did obtain in crystalline form the ethyl ester of (5-acetaminonaphthyl-1)-propionic acid. We did not carry our work any further in this direction.

The transition from (5-nitronaphthyl-1)-propionic acid to the diethylaminoethyl ester of (5-aminonaphthyl-1)-propionic acid was carried out by means of the methods usually practiced in such cases.

This alkamino ester was obtained by us in the form of its citrate, and as was to be expected, had no anaesthetic action.

EXPERIMENTAL

The ethyl ester of β -(5-nitronaphthyl-1)-dibromopropionic acid

In a round-bottomed flask, fitted with a reflux condenser with calcium chloride tube attached and a dropping funnel, there was placed 2 g of the ethyl ester of β -(5-nitronaphthyl-1)-acrylic acid, dissolved in 50 ml of dry chloroform. To the solution obtained there was gradually added from the dropping funnel 1.8 g of bromine, dissolved in 10 ml of chloroform. The addition of the bromine took place at room temperature.

After all the bromine had been added, the reaction mixture was allowed to stand for three days at room temperature. The chloroform was then distilled off in vacuum. The light yellow crystalline substance which remained was dissolved in ether. The ether solution was washed first with a 10% solution of sodium carbonate, then with water, dried with sodium sulfate, and the ether driven off. After the ether had been driven off there remained an almost colorless crystalline substance, which was recrystallized from 96% ethyl alcohol. Yield 2.4 g (75%).

The ethyl ester of β -(5-nitronaphthyl-1)-dibromopropionic acid was in the form of almost colorless, shining crystals with m.p. 147-148°. They were soluble upon heating in alcohol and acetone, more difficultly soluble in ether.

0.2155 g substance: 0.1804 g AgBr.

0.2244 g substance: 0.1958 g AgBr.

6.892 mg substance: 0.199 ml N_2 (18.5°, 747 mm).

0.735 mg substance: 0.185 ml N_2 (18.5°, 747 mm).

Found %: Br 37.36, 37.13; N 3.32, 3.16.

$C_{15}H_{13}O_4NBr_2$. Computed %: Br 37.09; N 3.25.

(5-Nitronaphthyl-1)-propionic acid

In a round-bottomed flask, fitted with a reflux condenser, 2.8 g of the ethyl ester of β -(5-nitronaphthyl-1)-dibromopropionic acid were dissolved in 75 ml. Bromination while heating resulted in tarring of the substance.

of absolute ethyl alcohol. Solution was carried out during heating on the water bath at the boiling point of alcohol. After all the material had dissolved, the solution was cooled to 35-40°, and there was added, drop by drop with stirring, a warm solution of 2.8 g of caustic potash in 12 ml of absolute ethyl alcohol. During this process, the rapid formation of potassium bromide was observed, and the formation of a redish-yellow color in the solution. When the reaction mixture was allowed to stand for 12-15 hours, a voluminous yellowish-greenish crystalline precipitate of the potassium salt of (5-nitronaphthyl-1)-propionic acid separated. This was filtered off. The filtrate was evaporated in vacuum without heating to $\frac{1}{3}$ its initial volume. During the evaporation a small additional amount of the potassium salt came out. This was added to the first precipitate and the combined precipitate was dissolved in water, the aqueous solution extracted several times with ether, filtered, and dilute sulfuric acid added to the filtrate until there was an acid reaction with Congo red. The (5-nitronaphthyl-1)-propionic acid was obtained in the form of an almost colorless amorphous precipitate, which was extracted with ether. The ether solution was washed once or twice with water, dried with sodium sulfate, and the ether driven off in vacuum without heating. The light yellow crystalline precipitate which remained was separated from the bromine-containing impurities. For this purpose the precipitate was first transferred into a small beaker, where it was washed with small quantities of ether, which were mixed with the precipitate. This operation was repeated many times, and the last washings were carried out directly on a filter. As the nitronaphthyl propionic acid is itself fairly soluble in ether, all the ether solutions obtained from the washing were collected together, and the ether was driven off in vacuum. The yellowish-white precipitate which remained was separated from bromine-containing impurities in a similar manner. After similar repeated washings with ether and subsequent recrystallizations with very gentle heating from chloroform, 0.65 g was obtained of a substance free from bromine (the presence of bromine was determined by the Beilstein test). This substance was in the form of an almost colorless powder, soluble in ether, acetone, alcohol, and chloroform upon heating, with m.p. 182-184° (with decomposition).** (The substance, in a sealed capillary, was placed in the apparatus for the determination of the melting point, which had been heated to 145-150°. The subsequent heating was carried out at a rate of 5 or 6° per minute. At 155° the substance partially sublimed, forming a colorless deposit in the upper part of the capillary. The residue in the capillary melted at 182-184°).

Analysis of the substance with m.p. 182-184°:

5.289 mg substance: 0.265 ml N₂ (19°, 746 mm).
 5.030 mg substance: 0.255 ml N₂ (19°, 749.5 mm).
 3.324 mg substance. 7.895 mg CO₂; 0.878 mg H₂O.
 3.024 mg substance. 7.184 mg CO₂; 0.789 mg H₂O.

Found %. N 5.75, 5.84; C 64.77, 64.79; H 2.92,
 C₁₂H₇O₄N. Computed %. N 5.81, C 64.73, H 2.91. 2.99.

The ethyl ester of (5-nitronaphthyl-1)-propionic acid

In a round-bottomed flask which was joined to a reflux condenser having a calcium chloride tube attached, there was placed 0.2 g of (5-nitronaphthyl-1)-propionic acid, 25 ml of absolute ethyl alcohol, and 0.05 ml of concentrated sulfuric acid (sp. gr. 1.84°). The reaction mixture was heated on the water bath at the

During subsequent washing it was observed that the yellowish color of the ether layer passed into the aqueous layer, from which a light precipitate was obtained by acidification with dilute sulfuric acid until there was an acid reaction to Congo Red. Then the precipitate again went into the ether layer.

** If the substance thus obtained is allowed to stand or is recrystallized from organic solvents with heating, its melting point gradually falls, and the analytical data, as the melting point falls more and more, deviate more and more from the results calculated for nitronaphthylpropionic acid.

boiling point of the alcohol for 8 hours. At the end of the reaction, the excess of alcohol was driven off and the residue poured into water and neutralized with a 10% solution of soda, then extracted with ether. The ether solution was washed with water, and dried with sodium sulfate, and the ether was distilled. The light yellow substance which remained was recrystallized twice from 96% ethyl alcohol.

The ethyl ester of (5-nitronaphthyl-1)-propionic acid was obtained in the form of shining light-yellow crystals with m.p. 121-122°, very soluble in ether, acetone, and ethyl alcohol.

4.970 mg substance: 0.217 ml N₂ (18.5°, 750.2 mm).

6.748 mg substance: 0.312 ml N₂ (18.5°, 752 mm).

Found %: N 5.05, 5.20.

C₁₅H₁₁O₄N. Computed %: N 5.10.

The ethyl ester of (5-acetamino-naphthyl-1)-propionic acid

In a three-necked round-bottomed flask, fitted with a stirrer and a reflux condenser, there was placed 0.7 g of the ethyl ester of (5-nitronaphthyl-1)-propionic acid, dissolved in 30 ml of 96% ethyl alcohol. The solution was heated to 57-60° and to it there was added 0.1 ml of concentrated hydrochloric acid (sp. gr. 1.19). Then, with stirring, there was gradually added 0.5 g of iron filings, and the stirring of the reaction mixture was continued for an additional 4 hours at the boiling point of the alcoholic solution. At the end of the reaction, the solution was filtered off from the inorganic precipitate, and the alcohol was driven off in vacuum. To the residue, a dark oily substance, 1 ml of acetic anhydride was added. Upon careful rubbing, the entire mixture turned into a light powder, which was recrystallized several times from 96% ethyl alcohol.

The ethyl ester of (5-acetaminonaphthyl-1)-propionic acid was in the form of almost colorless shining crystals with m.p. 183.5-184°, very soluble in alcohol and acetone, difficultly soluble in benzene, and almost insoluble in ether.

11.348 mg substance. 4.02 ml 0.01 N H₂SO₄ (Kjeldahl).

7.095 mg substance. 2.50 ml 0.01 N H₂SO₄.

Found %: N 4.96, 4.93.

C₁₇H₁₅O₃N. Computed %: N 4.97.

(5-Nitronaphthyl-1)-acetylene

In a round-bottomed flask joined to a reflux condenser there were placed 0.3 g of (5-nitronaphthyl-1)-propionic acid and 3 ml of pyridine. The reaction mixture was heated on the boiling water bath for 4 hours. At the end of the reaction the pyridine was driven off in vacuum. The yellow crystalline precipitate which remained was dissolved in ether. The ether solution was washed several times with a 10% solution of sodium carbonate, then with water, dried over sodium sulfate, and the ether driven off. The yellow crystalline precipitate was recrystallized several times from 96% ethyl alcohol. 0.1 g was obtained. The (5-nitronaphthyl-1)-acetylene was in the form of clear yellow crystals with m.p. 156-157°, very soluble in alcohol and ether. The substance had the characteristic property of acetylene of forming metallic compounds. Upon the addition of an ammoniacal solution of cuprous chloride to the alcoholic solution of nitronaphthylacetylene, an amorphous brick-colored precipitate was formed.

2.925 mg substance. 0.183 ml N₂ (21.5°, 745 mm).

3.520 mg substance. 0.214 ml N₂ (19°, 748 mm).

4.199, 3.022 mg substance. 11.289, 8.105 mg CO₂; 1.267, 0.983 mg H₂O.

Found %: N 7.11, 7.42; C 73.32, 73.15; H 3.38, 3.63

C₁₂H₇O₂N. Computed %: N 7.10, C 73.09, H 3.55

The hydrochloride of the β-diethylaminoethyl ester of (5-nitronaphthyl-1)-propionic acid

In a round-bottomed flask joined to a reflux condenser with calcium chloride

tube attached, there were placed 1 g of (5-nitronaphthyl-1)-propionic acid and 4 g of thionyl chloride. The mixture was heated on the water bath at the boiling point of the thionyl chloride for 6 hours. At the end of the reaction, the thionyl chloride was driven off in vacuum. The acid chloride of (5-nitronaphthyl-1)-propionic acid, which was left in the form of an oily substance, was dissolved in 50 ml of absolute benzene. To the solution obtained there was gradually added, with stirring, 0.6 g of freshly distilled diethylaminoethanol. The mixture obtained was heated on the water bath at the boiling point of the benzene solution for 3 hours. At the end of the reaction, the benzene was driven off in vacuum, and the hydrochloride of the diethylaminoethyl ester of (5-nitronaphthyl-1)-propionic acid, which remained in the form of a yellow crystalline substance, was dissolved in water. The aqueous solution was filtered, and from the filtrate, after the addition of a 10% solution of sodium carbonate, there precipitated the free alkamino ester base, which was extracted with ether. The ether solution was washed with water, dried with sodium sulfate, and filtered, and the ether was driven off. In order to remove traces of unreacted diethylaminoethanol, the oily material which remained after the ether had been driven off was heated in vacuum for an hour on the water bath, and then again dissolved in absolute ether. When the ether solution of the alkamino ester base was acidified with an ethereal solution of hydrogen chloride, the hydrochloride of the β -diethylaminoethyl ester of (5-nitronaphthyl-1)-propionic acid precipitated in the form of a light yellow crystalline substance, which was washed several times with dry ether, dried in a vacuum desiccator and recrystallized from absolute ethyl alcohol. Yield 0.7 g.

The hydrochloride of the β -diethylaminoethyl ester of (5-nitronaphthyl-1)-propionic acid was a yellow powder with m.p. 180-182°, very soluble in water and alcohol, soluble in benzene, chloroform, and acetone, insoluble in ether.

4.477 mg substance. 0.293 ml N₂ (22°, 725.8 mm).

4.633 mg substance. 0.295 ml N₂ (22°, 741.8 mm).

Found %: N 7.23, 7.18.

C₁₉H₂₀O₄N₂ HCl. Computed %: N 7.42.

The citrate of the β -diethylaminoethyl ester of (5-aminonaphthyl-1)-propionic acid

In a three-necked round-bottomed flask, fitted with a stirrer and a reflux condenser, there were placed 1.5 g of the hydrochloride of the β -diethylaminoethyl ester of (5-nitronaphthyl-1)-propionic acid, dissolved in 50 ml of 96% ethyl alcohol. The solution was heated to 57-60° and there were added to it, first 0.1 ml of concentrated hydrochloric acid (sp. gr. 1.19) and then, in a period of 1 hour, with careful mechanical stirring, 1 g of iron filings. The stirring was continued for 3 hours at the boiling point of the alcohol. After this, the solution was filtered free from the inorganic residue, and the alcohol was driven off in vacuum. The oily reaction product which remained was dissolved in water. To the aqueous solution of the alkamino ester hydrochloride, a 10% solution of sodium carbonate was added to precipitate the free alkamino ester base, which was extracted with ether. The ether solution was washed several times with water, dried with sodium sulfate, and filtered. To the filtrate there was added an alcoholic solution of citric acid. The oily precipitate which formed was filtered off, dried in a vacuum desiccator, and recrystallized from absolute ethyl alcohol. Yield 0.3 g.

The citrate of the β -diethylaminoethyl ester of (5-aminonaphthyl-1)-propionic acid was a grayish yellow powder, very soluble in water, alcohol, and acetone, soluble in benzene and chloroform, more difficultly soluble in carbon tetrachloride and ether.

The substance melted in an indefinite manner. At 80° it began to darken and sinter, toward 90° it liquefied and clung to the walls of the capillary, toward 135-140° it collected in the form of transparent drops.

7.270 mg substance: 0.370 ml N₂ (19.5°, 727.5 mm).
6.053 mg substance: 0.309 ml N₂ (20.7°, 727.5 mm).
Found %: N 5.69, 5.68.
C₂₅H₃₀O₉N₂. Computed %: N 5.57.

SUMMARY

1. (5-Nitronaphthyl-1)-propionic acid has been obtained by the bromination of the ethyl ester of β -(5-nitronaphthyl-1)-acrylic acid and the subsequent splitting off of the elements of hydrogen bromide from the ethyl ester of the β -(5-nitronaphthyl-1)-dibromopropionic acid.

2. (5-Nitronaphthyl-1)-propionic acid is easily decomposed to give carbon dioxide and (5-nitronaphthyl-1)-acetylene.

3. The diethylaminoethyl ester of (5-aminonaphthyl-1)-propionic acid has been obtained. This ester has no anaesthetic action.

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ON THE $\alpha, \alpha', \alpha''$ -TRIVINYLTRIALKYL ESTERS OF PHOSPHOROUS ACID

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The modern chemical literature has a detailed description of only a single representative of the complete esters of phosphorous acid which contain unsaturated radicals. In 1945, V.M.Zorcastrova, in her work carried out under the direction of A.E.Arbuzov, described the triallyl ester of phosphorous acid, synthesized by her by two methods. These were the reaction of the alcoholate of allyl alcohol with the acid chloride of allylphosphorous acid, and the method of preparation of the neutral esters of phosphorous acid developed by Milobendzsky and Sakhnovsky [1]. It was therefore of interest to obtain several new compounds of this class of organic derivatives of phosphorus in pure form, and to investigate their properties.

In order to obtain the complete esters of phosphorous acid with unsaturated radicals, we used the grignard reaction to prepare the following starting materials, all secondary unsaturated alcohols: methylvinyl carbinol, ethylvinyl carbinol, n-propylvinyl carbinol, n-butylvinyl carbinol, and phenylvinyl carbinol.

The reaction of phosphorous trichloride with the corresponding carbinols in absolute ether and dimethylaniline medium gave the following esters of phosphorous acid (Table 1):

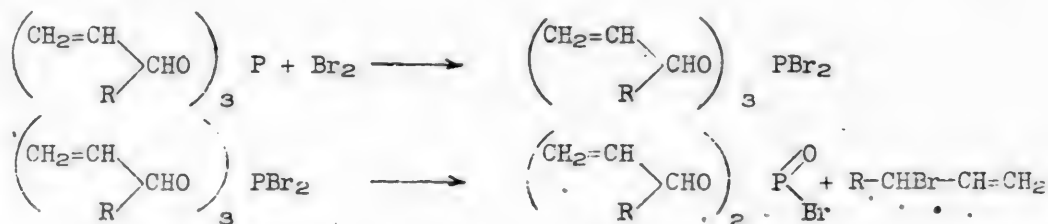
TABLE 1

Formula	B.p. at 9-15 mm	d	n_D
$\left(\begin{array}{c} \text{CH}_2=\text{CH} \\ \text{CH}_3 \end{array} \right) \text{CHO} \bigg)_3 \text{P} \dots$	92-93°	0.9557	1.4531
$\left(\begin{array}{c} \text{CH}_2=\text{CH} \\ \text{C}_2\text{H}_5 \end{array} \right) \text{CHO} \bigg)_3 \text{P} \dots$	123-124	0.9467	1.4521
$\left(\begin{array}{c} \text{CH}_2=\text{CH} \\ \text{C}_3\text{H}_7 \end{array} \right) \text{CHO} \bigg)_3 \text{P} \dots$	137-139	0.9365	1.4519
$\left(\begin{array}{c} \text{CH}_2=\text{CH} \\ \text{C}_4\text{H}_9 \end{array} \right) \text{CHO} \bigg)_3 \text{P} \dots$	156-157	0.9230	1.4521

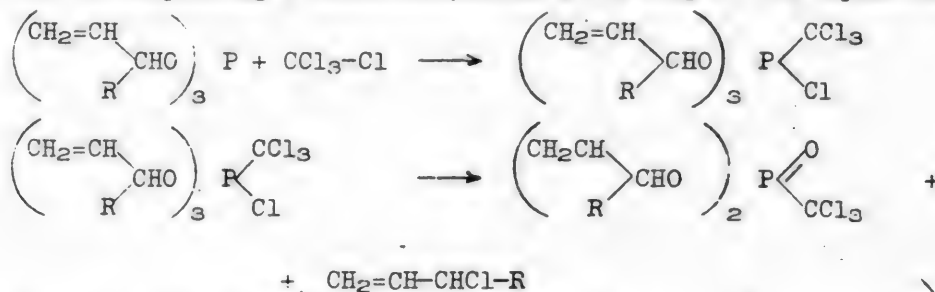
The isolated esters of phosphorous acid were oily, colorless liquids. They dissolved well in alcohol, ether, benzene, chloroform; reacted with cuprous halides with the evolution of heat and the formation of non-crystalline vitreous substances, they easily reacted with bromine, and they reacted upon heating with methyl iodide in carbon tetrachloride.

It is of interest to note that the ester of phosphorous acid obtained by the reaction of phenylvinyl carbinol with phosphorus trichloride did not distil even under high vacuum. When the temperature was raised to approximately 60°, the polymerization of the ester took place, with the evolution of a considerable amount of heat.

The experiments set up by us for the bromination of the $\alpha, \alpha', \alpha''$ -trivinyltrialkyl esters of phosphorous acid showed that the addition of bromine first took place normally, with the formation of a crystalline precipitate, but then, apparently, the formation of alkyl halides took place. The alkyl halides formed then added two more bromines to give 1,2,3-tribromoalkanes according to the following equations:



We further studied the action of carbon tetrachloride on the $\alpha, \alpha', \alpha''$ -trivinyltrialkyl esters of phosphorous acid. The experiments showed that the esters mentioned above reacted with carbon tetrachloride upon lengthy heating, with the formation of the corresponding 3-chloroalkylenes according to the equations:



However, the attempts to obtain the expected esters of trichloromethylphosphinic acid in pure form were not crowned with success.

The experiments we undertook on the Arbuzov isomerization of $\alpha, \alpha', \alpha''$ -trivinyltrialkyl esters of phosphorous acid with the corresponding alkylene halides led to the formation of undistillable syrupy substances.

EXPERIMENTAL

The starting materials, that is, the vinylalkyl carbinols, were obtained by the reactions of the corresponding alkylmagnesium bromides with acrolein [2]. The chief physical constants of these secondary carbinols are listed in Table 2.

The preparation of the ester with the composition $\left(\begin{array}{c} \text{CH}_2=\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CHO} \end{array} \right)_3 \text{P}$

In a round-bottomed flask with 500 ml capacity, fitted with a mechanical

TABLE 2

Formula	Boiling point	d_4^{20}	n_D
$\text{CH}_3\text{-CHOH-CH=CH}_2$	96-97°	0.8334	1.4139
$\text{C}_2\text{H}_5\text{-CHOH-CH=CH}_2$	112-116	0.8409	-
$\text{C}_3\text{H}_7\text{-CHOH-CH=CH}_2$	49-51 (20 mm)	0.8393	1.4230
$\text{C}_4\text{H}_9\text{-CHOH-CH=CH}_2$	63-64 (20 mm)	0.8384	1.4343
$\text{C}_6\text{H}_5\text{-CHOH-CH=CH}_2$	101-102 at 12 mm	1.0251	1.5406

stirrer, a reflux condenser, and a dropping funnel, there were placed 27 g of freshly distilled methylvinyl carbinol with b.p. 96-97°, 45.5 g of dimethylaniline, and 100 ml of absolute ether. To this mixture there was added, with good cooling and continuous stirring, 17.2 g of phosphorous trichloride. After the addition of the entire quantity of phosphorous trichloride, the cooling was discontinued. The reaction was considered complete after an hour and a half of additional stirring. The hydrochloride of dimethylaniline was then filtered off and washed twice with small amounts of absolute ether.

The ether was driven off from the filtrate in a current of carbon dioxide, and the remaining liquid was subjected to fractionation in a vacuum of 9 mm. The following fractions were obtained:

- I. B.p. to 86°, 0.83 g; and
- II. B.p. 86-93°, 24.72 g.

Another distillation of the second fraction gave a chief portion with b.p. 91-93° at 9 mm. Yield 15 g.

The ester obtained was a colorless oily liquid with a penetrating odor, soluble in organic solvents.

d_4^{20} 0.9557, n_D^{20} 1.4531, MR 69.02. $\text{C}_{12}\text{H}_{21}\text{O}_3\text{P}$ f. Computed: MR 69.33.

0.2416 g substance: 53.25 ml NaOH (1 ml NaOH = 0.5718 mg P)

0.2262 g substance: 49.21 ml NaOH.

Found %: P 12.61, 12.44.

$\text{C}_{12}\text{H}_{21}\text{O}_3\text{P}$. Computed %: P 12.71.

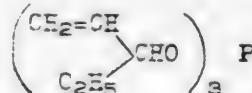
The ester, as a derivative of trivalent phosphorus, reacted with cuprous bromide, methyl iodide, and carbon tetrachloride. The reaction of carbon tetrachloride on the ester gave 3-chlorobutene-1.

The bromination of α,α',α' -trivinyltriethyl phosphite.

To 8 g of α,α',α' -trivinyltriethyl phosphite, dissolved in 50 ml of ethyl ether, there was added drop by drop, with good cooling, 15 g of bromine. At first the reaction was accompanied by the evolution of a considerable amount of heat. After the solvent had been driven off, the oil which remained was subjected to distillation in vacuum. Distillation gave a product with b.p. 113-114° at 21 mm. The mass that remained in the flask did not distil over, and upon cooling did not crystallize.

Judging from its other properties, the product with b.p. 113-114° at 12 mm corresponded to 1,2,3-tribromobutane [3].

The preparation of the ester with the composition



The preparation of the ester was carried out in a manner similar to the one above, but the dimethylaniline was replaced by diethylaniline.

From 26.6 g of ethylvinyl carbinol, 51.5 g of diethylaniline, and 14.2 g

of phosphorus trichloride in absolute ether medium, the $\alpha, \alpha', \alpha''$ -triethyltriallyl phosphite was obtained.

B.p. 102-103° at 3 mm and 123-124° at 10 mm. Yield 24.8 g of substance, or about 84% of theory.

The ester obtained was an oily liquid with a mild unpleasant odor.

d_4^{20} 0.9467; n_D^{20} 1.4521.

0.1566 g substance: 30.1 ml NaOH (1 ml NaOH 0.5546 mg P).

0.1443 g substance: 28.6 ml NaOH.

Found %: P 10.66, 10.99.

$C_{15}H_{27}O_3$. Computed %: P 10.84.

The ester reacted easily with methyl iodide and carbon tetrachloride with the formation of products which could not be distilled without decomposition at a pressure of 1 mm.

The bromination of the ester with the composition $\left(\begin{array}{c} CH_2=CH \\ C_2H_5 \end{array} \right) CHO \right)_3 P$

To a solution of 7.5 g (1 mole) $\alpha, \alpha', \alpha''$ -triethyltriallyl phosphite in 50 ml of absolute ether 16.7 g of bromine (4 moles) were added, with cooling by snow. The first drops of bromine reacted with the evolution of considerable heat and the formation of a white crystalline precipitate, which gradually went into solution as more and more bromine was added. After the addition of the entire amount of bromine, the solvent was driven off. The residue was subjected to fractionation in vacuum in a stream of carbon dioxide. This gave a fraction with b.p. 118-120° at 20-21 mm, but then most of the residue did not distil but underwent vigorous decomposition.

According to the analytical data, the substance was pure 1,2,3-tribromopentane. It was a colorless liquid with a camphor odor.

d_4^{20} 2.0213; n_D^{20} 1.5540; MR 48.64.

$C_5H_9Br_3$. Computed. MR 48.59.

0.1769 g substance: 0.3220 g AgBr.

0.1316 g substance: 0.2396 g AgBr.

Found %: Br 77.48, 77.46.

$C_5H_9Br_3$. Computed %: Br 77.63.

The preparation of the ester with the composition $\left(\begin{array}{c} CH_2=CH \\ C_3H_7 \end{array} \right) CHO \right)_3 P$

The reaction of 7.9 g of propylvinylcarbinol, 11.8 g of diethylaniline, and 3.7 g of phosphorus trichloride in absolute ether medium (50 ml) gave $\alpha, \alpha', \alpha''$ -tripropyltriallyl phosphite. B.p. 137-139° at 13 mm.

The ester obtained was a colorless oily liquid which easily reacted with methyl iodide and carbon tetrachloride.

d_4^{20} 0.9365; n_D^{20} 1.4519.

0.1154 g substance: 20.2 ml NaOH (1 ml NaOH 0.5546 mg P).

0.1518 g substance: 25.5 ml NaOH.

Found %: P 9.38, 9.32.

$C_{19}H_{33}O_3P$. Computed %: P 9.46.

The preparation of the ester with the composition $\left(\begin{array}{c} CH_2=CH \\ C_4H_9 \end{array} \right) CHO \right)_3 P$

$\alpha, \alpha', \alpha''$ -trivinyltriallyl phosphite was obtained from 27 g of n-butylvinyl carbinol, 28.65 g of freshly distilled dimethylaniline, and 11 g of phosphorus

trichloride in 100 ml of absolute ether. B.p. 155-157° at 15 mm. Yield about 63% of theory.

The ester obtained was a transparent oily liquid with a characteristic odor, soluble in ether, alcohol, and other organic solvents.

d_4^{20} 0.9400, d_6^{20} 0.9230; n_D^{20} 1.4521.

0.1786 g substance: 27.1 ml NaOH (1 ml NaOH 0.5686 mg P).

0.1906 g substance: 28.9 ml NaOH.

Found %: P 8.62, 8.61.

$C_{21}H_{39}O_3P$. Computed %: P 8.38

The action of carbon tetrachloride on α,α',α'' -trivinyltrialkyl phosphite

To 6 g of α,α',α'' -trivinyltrialkyl phosphite 2.5 g of carbon tetrachloride was added drop by drop. After 2 hours of heating, the reaction products were subjected to fractionation in a current of carbon dioxide. A substance was obtained with b.p. 104-107° at ordinary pressure. The residue in the flask did not distill even at a pressure of 1 mm.

The substance obtained, 3-chloropentene, was a transparent liquid.

d_4^{20} 0.9484; d_6^{20} 0.9284; n_D^{20} 1.4501.

0.1598 g substance: 0.1707 g AgCl.

Found %: Cl 26.43.

$C_7H_{13}Cl$. Computed %: Cl 26.75.

The bromination of α,α',α'' -trivinyltrialkyl phosphite.

6 g of α,α',α'' -trivinyltrialkyl phosphite was mixed with 20 ml of absolute ether, and to the mixture there was slowly added, with cooling, 10.5 g of bromine. After the solvent had been driven off, the residue was distilled in vacuum.

The boiling point of the chief fraction was 136-138° at 12 mm. A viscous mass with a dark color remained in the distilling flask. This did not crystallize even upon long standing.

The 1,2,3-tribromoheptane was a colorless liquid.

d_4^{20} 1.7805; d_6^{20} 1.7519; n_D^{20} 1.5361.

0.2088 g substance: 0.3486 g AgBr.

0.1605 g substance: 0.2689 g AgBr.

Found %: Br 71.05, 71.30.

$C_7H_{13}Br_3$. Computed %: Br 71.17.

The action of phosphorus trichloride on phenylvinyl carbinol.

To a mixture of 60 g of phenylvinyl carbinol, 66.7 g of diethylaniline, and 200 ml of absolute ether, 20.5 g of phosphorus trichloride was added with cooling. The diethylaniline hydrochloride that precipitated was filtered off and washed twice with ether. The ether was driven off from the filtrate in a current of carbon dioxide, and the residual liquid in the flask was subjected to vacuum distillation. But at a temperature of about 60° a stormy decomposition began, with the evolution of heat. Then the entire mass polymerized to give a yellowish solid mass.

The rest was treated with bromine. 5.7 g of the undistilled product from the carbinol - phosphorus trichloride reaction was dissolved in 40 ml of absolute ethyl ether, and to this mixture 8.5 g of bromine was added. The crystals which precipitated were filtered. After recrystallization from alcohol, the crystals had m.p. 123-124°.

0.1223 g substance: 0.1934 g AgBr.
Found %: Br 67.25.
 $C_9H_9Br_3$. Computed %: Br 67.19.

Analysis of the crystals confirmed the fact that the substance obtained was 1,2,3-tribromopropylbenzene [4].

SUMMARY

1. New $\alpha, \alpha', \alpha''$ -trivinyltrialkyl esters of phosphorous acid have been synthesized and studied.
2. The esters obtained, as derivatives of trivalent phosphorus, reacted with cuprous salts, with methyl iodide, and with carbon tetrachloride.
3. It has been found that the bromination of $\alpha, \alpha', \alpha''$ -trivinyltrialkyl esters of phosphorous acid gives 3-chloroalkenes. Attempts to obtain the esters of trichloromethylphosphinic acid were not crowned with success.

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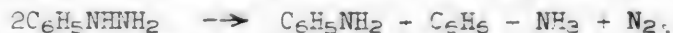
XXVIII. A COMPARISON OF THE ACTIVITIES OF AMMONIA AND ANILINE IN THE REACTION WITH FURAN AND FURANIDINE

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In preceding papers it has been shown that the reaction of furan or furanidine (tetrahydrofuran) with ammonia, or with primary aliphatic, aromatic, or heterocyclic amines in the presence of aluminum oxide at high temperature gives pyrrol, pyrrolidine, or the corresponding N-substituted pyrrols or pyrrolidines [1].

It was of interest to study the comparative activities of ammonia and aniline both during their simultaneous reactions with furan or furanidine, and during the action of a mixture of ammonia and aniline at the moment of their simultaneous formation. In order to carry out this latter reaction, we used phenylhydrazine, which, both in an autoclave at 300° [2], and above aluminum oxide at 400°, decomposes to give aniline, benzene, ammonia, and nitrogen:



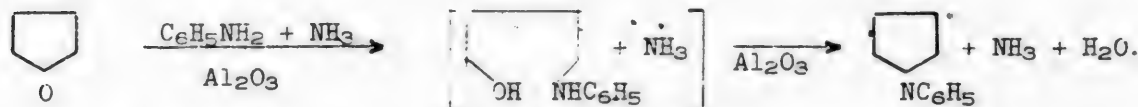
In the present work it was found that when mixtures of ammonia and aniline react with furan, N-phenylpyrrol is obtained (yield 18% of the theoretical), and only traces of pyrrol are formed. Similar results were obtained when mixtures of ammonia and aniline were made to react with furan at the moment of their formation, i.e., when furan reacted with phenylhydrazine (1:2), and in this case too N-phenylpyrrol was obtained (yield 10% of the theoretical), while here the presence of pyrrol could be found only qualitatively (by its reaction on a pine splinter) in a fraction that, to judge from its boiling point, had very little pyrrol.

The reaction of a mixture of ammonia and aniline with furanidine led to the formation only of N-phenylpyrrolidine (yield 22.5% of the theoretical). A similar result was obtained in the reaction of furanidine with phenylhydrazine (1:2). N-phenylpyrrolidine was the chief product of reaction (yield 23% of the theoretical). Pyrrolidine itself was observed in only negligible quantities, and was identified as the picrate. The use of an excess of phenylhydrazine in the reaction with furanidine (in molar ratios of 1:3, 1:4) lowered the yields of N-phenylpyrrolidine and also led to the formation of carbazole as a byproduct of the reaction. The results obtained are listed in the table.

The data listed in the table show the selective course of the reaction which led chiefly to the formation of N-phenylpyrrol or N-phenylpyrrolidine.

The reaction of furan and furanidine with mixtures of ammonia and aniline

Expt. No.	Starting material		Molar ratio of reagents	Products of reaction		Note
				Name	Yield (% of theory)	
1	Furan	Ammonia and aniline	1:1.1	N-phenylpyrrol Pyrrol	18 Traces	-
2	Furan	Ammonia and aniline (from phenylhydrazine)	1:1.1	N-phenylpyrrol Pyrrol	10 Traces	-
3	Furanidine	Ammonia and aniline	1:1.1	N-phenylpyrrolidine	22.5	-
4	Furanidine	Ammonia and aniline (from phenylhydrazine)	1:1.1	N-phenylpyrrolidine Pyrrolidine	23 Traces	-
5	Furanidine	Same	1:1.5:1.5	N-phenylpyrrolidine	7	Small amount of carbazole
6	Furanidine	Same	1:2:2	N-phenylpyrrolidine	5.0	Same



This course of the reaction is to be explained by the fact that aniline is a weaker base than ammonia (the ionization constant for aniline is 4.58, for ammonia 9.27 [5]), and as a result of this, the rupture of the polar carbon-oxygen bond in furan (the dipole moment of furan in benzene at 25° equals 0.71 D [4]) and especially in furanidine (the dipole moment of furanidine in benzene at 25° equals 1.71 D [4]) takes place more easily in the case of these oxygen-containing heterocycles with aniline than with ammonia.

EXPERIMENTAL

The decomposition of phenylhydrazine. 22.6 g of phenylhydrazine was passed in a weak current of nitrogen, with a velocity of 5 or 6 drops per minute, over aluminum oxide, heated to 400°. The catalysate was collected with good cooling of the receiver. For a quantitative determination of the ammonia formed, the exit tube of the receiver was joined to an absorption flask containing 32 ml of 3.39 N sulfuric acid solution. At the end of the reaction the acid was titrated with 16.3 ml of 0.789 N NaOH solution. Therefore, 1.7 g of ammonia (96% of the theoretical) was formed. When the catalysate was dried with fused caustic potash and distilled there were obtained: 5 g of benzene (yield 61% of the theoretical), b.p. 79-80° (750 mm), n_D^{20} 1.5008, d_4^{20} 0.8901, and 7 g of aniline (yield 72% of the theoretical), b.p. 60-61° (8 mm), n_D^{20} 1.5848, d_4^{20} 1.0215.

The reaction of furan with a mixture of ammonia and aniline A mixture of 15 g of furan and 20 g of aniline (molar ratio 1:1) was led over aluminum oxide at 450° with a velocity of 6 to 8 drops per minute in a current of ammonia. The velocity of the ammonia was so regulated that the molar ratio of aniline and ammonia was 1:1. The catalysate, collected in a well-cooled receiver, was extracted

with ether. The ether extract was dried with fused caustic potash, and the ether driven off. A distillation of the reaction product gave 0.7 g of pyrrol fraction with b.p. 127-132° and n_D^{20} 1.5051. This gave an intense pyrrol reaction with a pine splinter moistened with concentrated hydrochloric acid. There was also 11 g of aniline (52% of the amount used in the reaction) with b.p. 56-58° (3 mm); and 5.5 g of N-phenylpyrrol (yield 18% of the theoretical), with b.p. 94-95° (3 mm), m.p. 61-62°.

The literature gives for pyrrol. Nasini and G. Carrara [5] n_D^{21} 1.50468, d_4^{21} 0.9669; J. Brühl [6] - B.p. 128-129° (751.9 mm); $n_D^{19.7}$ 1.50347; d_4^{20} 0.9481; Yu. K. Yuryev [1] - B.p. 130-131° (760 mm), n_D^{20} 1.5091, d_4^{20} 0.9480.

The literature gives for N-phenylpyrrol: Kottwitz [7] M.p. 62°; A. Pictet and P. Crepieux [8] - B.p. 234°, Yu. K. Yuryev [1] M.P. 61-62°.

The reaction of furan with phenylhydrazine. 15 g of furan, dissolved in 47.5 g of phenylhydrazine (molar ratio 1.2) was passed with a velocity of 6 to 8 drops per minute over aluminum oxide heated to 450°. After the passage of each 20 or 21 g of the mixture, the catalyst was regenerated. The treatment of the catalysate as indicated above gave 11 g of benzene, b.p. 76-78° (757 mm), 0.2 g of a pyrrol fraction with b.p. 130-134° (757 mm), n_D^{20} 1.5072, which gave an intense pyrrol reaction with a pine splinter moistened with concentrated hydrochloric acid, 14 g of aniline (yield 68% of the theoretical), b.p. 59-62° (5 mm). The residue from the distillation crystallized. Upon recrystallizing it from aqueous alcohol, 3 g of N-phenylpyrrol was obtained (10% of the theoretical), with m.p. 61°.

The reaction of furanidine with a mixture of ammonia and aniline. A mixture of 16 g of furanidine and 21 g of aniline (molar ratio 1.1) was passed with a velocity of 8 to 10 drops per minute over aluminum oxide at 400° in a current of ammonia. The catalysate was collected in a receiver cooled with a mixture of snow and salt. After the ether extract had been dried with fused caustic potash, and the ether had been driven off, there were obtained 14.8 g of aniline (70% of that used for the reaction), b.p. 73-76° (11 mm), n_D^{20} 1.5808, 7.3 g of N-phenylpyrrolidine (yield 22.5% of the theoretical), b.p. 109-111° (8 mm); n_D^{20} 1.5792, d_4^{20} 1.0152, MR_D 46.20 (computed for $C_{10}H_{13}N$ MR_D 46.51), EM_D 1.69. m.p. of the picrate 116°.

The literature gives for N-phenylpyrrolidine: J. Braun and G. Lemke [9] - B.p. 124° (14 mm), F. Signaigo and H. Adkins [10] - B.p. 110-116° (9 mm); d_4^{25} 1.021, n_D^{25} 1.5803, m.p. picrate 115-116°, Yu. K. Yuryev [1] - B.p. 114° (9 mm); d_4^{20} 1.0183, n_D^{20} 1.5853, EM_D 1.86, m.p. of picrate 116°.

Pyrrolidine, which might have been formed as a result of the reaction of the furanidine with ammonia, was not observed at all.

The reaction of furanidine with phenylhydrazine. Experiment No. 1. A mixture of 12.5 g of furanidine and 37.5 g of phenylhydrazine (molar ratio 1.2) was led with a velocity of 6 to 8 drops per minute in a gentle current of nitrogen over aluminum oxide, heated to 400°. After each 15 to 17 g of the mixture was passed over it, the catalyst was regenerated. The ether extract of the catalysate was dried with fused caustic potash, the ether was driven off, and the catalysate residue distilled. 7 g of benzene came over, b.p. 77-79° (755 mm), with a sharp odor of pyrrolidine. In order to remove the pyrrolidine, the benzene fraction was washed with a 2 N solution of hydrochloric acid. The hydrochloric acid solution was evaporated on the water bath, and the residue treated with a 40% solution of caustic potash and extracted with ether. Upon the addition to the ether solution of a saturated ether solution of picric acid, pyrrolidine picrate was obtained. After recrystallization from alcohol it melted at 111°.

The literature gives for pyrrolidine picrate: S. Gabriel [11] - m.p. 112-113°, Yu. K. Yuryev [1] - m.p. 111-112°.

The benzene, freed from pyrrolidine, washed, and dried, distilled at 80° (758 mm) and had n_D^{20} 1.5000 and d_4^{20} 0.8740. The catalysate residue (after the removal of the benzene from it) was distilled in vacuum. There were obtained: 11 g of aniline (yield 62.5% of the theoretical), b.p. 73-74° (12 mm), n_D^{20} 1.5864, d_4^{20} 1.0216, and 6.5 g of N-phenylpyrrolidine with b.p. 122-125° (12 mm).

After purification with p-toluenesulfonylchloride [12], the N-phenylpyrrolidine had the following constants: b.p. 124-125° (12 mm); n_D^{20} 1.5860, d_4^{20} 1.0182; MR_D 48.52 ($C_{10}H_{13}N$ 3. Computed MR_D 46.51); EM_D 2.01. Yield 6 g (23.5% of the theoretical).

Experiment No. 2. A mixture of 15 g of furanidine and 67 g of phenylhydrazine (molar ratio 1.5) was made to react at 400°. After the corresponding treatment of the catalysate, there were obtained: 13 g of benzene, b.p. 79-80° (760 mm); n_D^{20} 1.5060; 21 g of aniline (yield 72% of the theoretical), b.p. 73-75° (12 mm) with n_D^{20} 1.5865, 2.2 g of N-phenylpyrrolidine (yield 7.0% of the theoretical), b.p. 122-124° (12 mm); n_D^{20} 1.5840. After the N-phenylpyrrolidine had distilled off in the interval 160-180° (10 mm), 3 g of carbazole distilled over. After recrystallization from chloroform, the carbazole was obtained in the form of white crystals with a mother of pearl luster, m.p. 234-236°. A mixed test showed no depression of the melting point; m.p. 235-237°.

3.608 mg substance: 0.259 ml N_2 (21°, 759 mm).

2.903 mg substance: 0.212 ml N_2 (20°, 756 mm).

Found % N 8.32, 8.48.

$C_{12}H_9N$. Computed % N 8.58.

The literature gives for carbazole; O. Zeidler [13] - m.p. 245°; C. Graebe [14] - m.p. 238°; W. Kirby [15] m.p. 247°, b.p. 351.5°.

Experiment No. 3. A mixture of 10 g of furanidine and 60 g of phenylhydrazine (molar ratio 1.4) was made to react at 400°. After the corresponding treatment of the catalysate, there were obtained: 14.4 g of benzene, b.p. 79-80° (758 mm); n_D^{20} 1.4995; 22 g of aniline (yield 84% of the theoretical), b.p. 73-75° (12 mm); n_D^{20} 1.5850; 11 g of N-phenylpyrrolidine (yield 5% of the theoretical, b.p. 122-124° (13 mm), n_D^{20} 1.5865, a small amount of carbazole with m.p. 236-238°. A mixed test showed no depression of the melting point; m.p. 236-238°.

SUMMARY

The results obtained in the study of the comparative activity of ammonia and aniline both when they were allowed to react simultaneously with furan or furanidine, and when a mixture of them was allowed to react at the moment of their simultaneous formation from phenylhydrazine, permits us to draw the following conclusions.

1. The reaction of furan with mixtures of ammonia and aniline gives N-phenylpyrrol, and only traces of pyrrol are observed in addition to this.

2. The reaction of furanidine with mixtures of ammonia and aniline gives N-phenylpyrrolidine, and only traces of pyrrolidine are observed.

3. The selectivity of the course of the reactions described, which leads to the formation of N-phenylpyrrol and N-phenylpyrrolidine, is to be explained most easily by a rupture of the polar carbon-oxygen bond in furan and furanidine under the action of aniline, which is the weaker of the bases used for the reaction.

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ON 1,3-DIMETHYLCYCLOPENTANE

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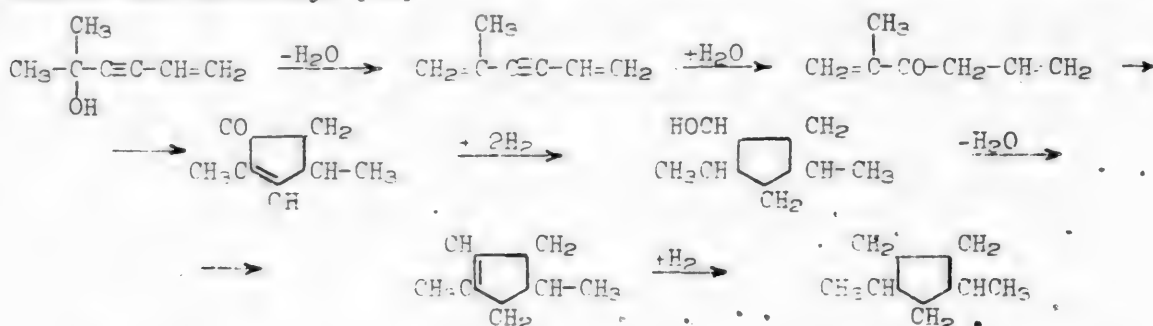
1,3-Dimethylcyclopentane was synthesized for the first time in 1896 by N. D. Zelinsky and M. Ruzsky [1] from α, α' -dimethyladipic acid by way of 2,5-dimethylcyclopentanone-1. Later [2], N. D. Zelinsky obtained this hydrocarbon from optically active 1,3-dimethylcyclopentanol-1, and inasmuch as the hydrocarbon also showed optical activity, ascribed to it the structure of the trans isomer. In 1926, Chavanne [3] obtained 1,3-dimethylcyclopentane starting from 1-methylcyclohexanol-4, by way of β -methyladipic acid, β -methylcyclopentanone, the tertiary alcohol (by the Grignard reaction) and the unsaturated hydrocarbon. Later on this hydrocarbon was synthesized in the same way by Evans [4] and by Kazansky and Rumyantseva [5]. All the preparations of 1,3-dimethylcyclopentane obtained up to the present time have similar physical properties and distill within narrow limits. In contradistinction to 1,2-dimethylcyclopentane, which has been separated into cis and trans isomers which have been well characterized at the present time, 1,3-dimethylcyclopentane is usually regarded as a homogeneous hydrocarbon, although in late years there have been several attempts to obtain it in two stereoisomeric forms. Thus, in 1942 Mousseron and Granger [6] described the synthesis and separation of cis-trans-1,3-dimethylcyclopentanes. However, the constants of the isomers reported by them differed so sharply from the properties of this hydrocarbon hitherto indicated in the literature, that serious doubt necessarily arose about the data given by the French chemists. In 1947 Birch and Oldham [7] attempted to obtain cis-1,3-dimethylcyclopentane from cis-cyclopentane-1,3-dicarboxylic acid by the reduction of its ester to cis-1,3-di-(hydroxymethyl)-cyclopentane, then substituting the hydroxyls in this compound by halogen, and converting the dihalogen-derivative into the hydrocarbon. However, this last compound appeared from its properties to be identical with the 1,3-dimethylcyclopentane (trans form?) which had been more than once described. Finally, in the same year, Fenske, together with a number of other authors [8], in a paper devoted to the Raman spectra of hydrocarbons, listed data for the cis and trans isomers of 1,3-dimethylcyclopentane, without giving any method for preparing and separating them, and without giving data to characterize the degree of purity of the isomers. The difference in their boiling points amounted in all to 1°, and the values of the indices of refraction were extraordinarily close.

Thus, the question of the synthesis and properties of stereoisomeric 1,3-dimethylcyclopentanes cannot at the present time be considered decisively settled, and we were forced to assume that this hydrocarbon could in general exist in the form of only a single geometrical isomer, or that the majority of the preparations obtained up to the present time were mixtures with extraordinarily close physical properties, and therefore were stereoisomers extremely difficult to separate. We

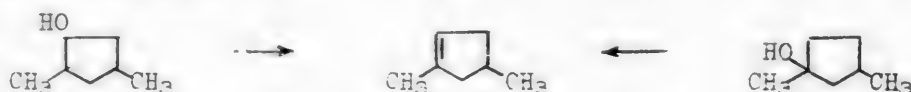
must note that the other known homologs of cyclopentane containing two alkyl substituents in positions 1 and 3 have also been described in only a single form, while the 1,2-dialkylated cyclopentanes have in the majority of cases been successfully separated into cis and trans forms.

Recently, using the I.N. Nazarov reaction of cyclization-hydration of the dienines [9], we obtained 1,2,3-trimethylcyclopentane and separated it into three stereoisomers [10,14]. During this it appeared that the conditions of hydrogenation of the trisubstituted cyclopentenones obtained at a certain stage of this complicated synthesis to a considerable degree influenced the relative amounts of geometric isomers formed, in accordance with the rule of Auwers and Skita [11]: upon hydrogenation in acid medium, the amount of cis-isomer formed increased.

In the present paper we shall describe the synthesis of 1,3-dimethylcyclopentane, starting with 2-methylhexen-5-in-3-ol-2 (dimethylvinylethynyl carbinol), by means of the corresponding cyclopentene and the dimethylcyclopentenone described by Nazarov and Zaretskaya [12].



We shall assume that in the dehydration of 2,4-dimethylcyclopentanol-1 there are obtained not the two possible dimethylcyclopentenones with different positions of the double bond, but one, namely, 2,4-dimethylcyclopentene-1, on the ground that as is evident from the work of Kazansky, Koperina, and Zemskaia [13], the dehydration of the 1,3-dimethylcyclopentanol-1 synthesized by the Grignard reaction gives a dimethylcyclopentene with completely identical properties. Obviously this hydrocarbon can be only 2,4-dimethylcyclopentene-1, as can be seen from the following equations.



The hydrogenation of the dimethylcyclopentenone and the dimethylcyclopentene formed as intermediate products led, as in the work just cited, to the production of 1,2,3-trimethylcyclopentane, both in acid and in neutral medium. However, no difference was observed in the properties of the 1,3-dimethylcyclopentane preparations obtained in respect to this, despite the fact that we might have expected the formation of both an alcohol and a saturated cyclic hydrocarbon in stereoisomeric forms. Thus, the present work also does not decide the question of the stereoisomerism of 1,3-dimethylcyclopentane.

EXPERIMENTAL

1. The synthesis of 2,4-dimethylcyclopentene-2-one-1. As the starting material we used technical 2-methylhexen-5-in-3-ol-2 (dimethylvinylethynyl carbinol), from which we selected the fraction with b.p. 60° (20 mm). It was dehydrated with 50% sulfuric acid by heating to 50-60°, and gave 5-methylhexadien-1,5-in-3 in yields of 66-70%. This distilled at 45-47° (85 mm) and had n_D^{20} 1.4960. The dienine was then hydrated by heating with a mixture of sulfuric acid and mercuric sulfate in 90% methanol solution. A mixture of ketone and methoxyketones (not indicated in the mechanism of the reaction given above) was obtained, with

a boiling range from 63 to 100° (15 mm). The mixture was cyclized without separation of the ketone by heating with phosphoric acid (sp. gr. 1.73) to give 2,4-dimethylcyclopenten-2-one-1 in a yield 47% of theory, based on the diene used. The unsaturated cyclic ketone had b.p. 71-73° (25 mm) and n_D^{20} 1.4670.

2. The hydrogenation of 2,4-dimethylcyclopenten-2-one-1. a) In acid medium at normal pressure in the presence of platinized carbon. We shall give a description of a typical experiment. In a duck-shaped glass hydrogenation vessel there were placed 30 g of the unsaturated ketone, 50 ml of ethyl alcohol, 1 g of powdered platinized carbon (20% Pt), and 4 ml of a solution of chloroplatinic acid (0.1 g Pt in 1 ml). The absorption of hydrogen at first took place very rapidly at room temperature, but gradually slowed down, and was not accelerated by the addition of 0.5 g of fresh platinized carbon and 0.5 ml of chloroplatinic acid solution. A total of 12.9 liters of hydrogen was absorbed (0°, 760 mm), which amounted to 2.1 moles of hydrogen per mole of ketone to be hydrogenated. In other hydrogenation experiments, which we shall not describe in detail, the same features were observed.

After hydrogenation, the alcoholic solutions were filtered, the catalyst carefully washed with alcohol, the filtrates united, and the alcohol driven off from a Favorsky flask. The saturated hydrocarbon formed was driven off along with the alcohol, and could be separated by diluting the alcoholic distillate with water. After freeing it from traces of unsaturated compounds by shaking with concentrated sulfuric acid, further purifying it, and drying, the hydrocarbon was distilled in the presence of metallic sodium in a column with the equivalent of 30 theoretical plates. During the distillation, the hydrocarbon boiled completely at a single point and had these properties: b.p. 90.5° (751 mm); n_D^{20} 1.4094; d_4^{20} 0.7457; M_R 32.56 (computed for C_7H_{14} 32.33), aniline point 48.5°.

From 80 g of the ketone a total of 17.2 g of the hydrocarbon was obtained, amounting to 24% of theory, calculated on the basis of the unsaturated ketone.

After the ethyl alcohol had been driven off, the distillation of the other hydrogenation products began, that is of the saturated cyclic alcohol, 2,4-dimethylcyclopentanol-1. It had b.p. 159-161° (750 mm), n_D^{20} 1.4418, and d_4^{20} 0.8902. From 80 g of the unsaturated ketone, a total of 49.4 g of the alcohol was obtained, amounting to about 60% of theory. After the distillation, a viscous tarry mass remained in the flask.

It is of interest to note that the reduction of 2,4-dimethylcyclopenten-2-one-1 under these conditions to the saturated alcohol takes place much more easily than the reduction of 2,3,4-trimethylcyclopenten-2-one-1 to the alcohol. In the latter case, the reaction proceeds easily to give the saturated ketone, and with considerably less speed to give the saturated alcohol, while among the reduction products of 2,4-dimethylcyclopenten-2-one-1 we observed no saturated ketone (reaction with semicarbazide). When there was insufficient absorption of hydrogen, we found the unsaturated cyclic ketone along with the saturated cyclic alcohol.

b). Hydrogenation in an autoclave under pressure with hydrogen in the presence of Raney nickel. 56 g of freshly distilled 2,4-dimethylcyclopenten-2-one-1, 100 ml of ethyl alcohol, and 5 g of catalyst were immersed in a rotating autoclave with a capacity of 450 ml. At the beginning, with a hydrogen pressure of 100 atm., the gas was quickly absorbed even at 20°, and only toward the end of the hydrogenation did the temperature inside the autoclave have to be raised to 85°. A total of about 2 moles of hydrogen were absorbed per 1 mole of unsaturated ketone used. The alcoholic solution was filtered and the catalyst washed with alcohol. The alcoholic solutions were united, and the alcohol driven off in a Favorsky flask. But when the alcoholic distillate was diluted with water,

in contradistinction to what has been described in section (a), only oily drops separated, which we were unable to investigate. After the ethyl alcohol had been driven off, the temperature of the vapor rose sharply to 154°, and the distillation of 2,4-dimethylcyclopentanol-1 began. It distilled from 155 to 157° (737 mm) and had n_D^{20} 1.4473. Its yield was 49.5 g, which amounted to 85.3% of theory, based on the unsaturated ketone.

3. The dehydration of 2,4-dimethylcyclopentanol-1. The two portions of 2,4-dimethylcyclopentanol-1, obtained by the hydrogenation of the unsaturated ketone with platinized carbon and with Raney nickel in an autoclave, were dehydrated separately by heating with crystalline oxalic acid (50 g of the alcohol, 100 g of the acid) on an oil bath at 115° for 2.5 hours. After this the temperature of the bath was raised, and at 135-140° the mixture of unsaturated hydrocarbon and water was distilled off. Water was added to the residue in the flask, and the distillation repeated. The distillates from these two distillations were combined, and the hydrocarbon separated from the water layer, washed with a dilute solution of alkali, dried, and distilled. The yield of unsaturated hydrocarbon from dehydration of the alcohol amounted to 78-81%.

Both the alcohol obtained by hydrogenation with platinized carbon in acid medium and the alcohol obtained by hydrogenation in an autoclave with Raney nickel in neutral medium gave an unsaturated hydrocarbon with identical properties, as can be seen from the following (Table 1).

TABLE 1

Conditions for preparation of original alcohol	Properties of hydrocarbon obtained			
	Boiling point	Pressure, mm Hg	n_D^{20}	d_4^{20}
Hydrogenation with platinum in acid medium	91.8-92.8°	757	1.4283	0.7702
Hydrogenation with nickel in neutral medium	91.5-92.5°	750	1.4282	0.7702

The two preparations were mixed, and the mixture was distilled in a column with the equivalent of 30 theoretical plates. After a very small preliminary fraction, everything else distilled within a range of 0.1°; this indicated the complete identity of the two preparations. The hydrocarbon obtained had a b.p. 92.7-92.8° (750 mm), n_D^{20} 1.4288; d_4^{20} 0.7714, MR_D found 32.10, computed for C_7H_{12} 31.86.

The dimethylcyclopentene obtained by the dehydration of the 1,3-dimethylcyclopentanol-1 (synthesized by the Grignard reaction) had the same properties. B.p. 92.7° (751 mm); n_D^{20} 1.4287; d_4^{20} 0.7715 [13], i.e., it must have had the same structure, which could only be the one described.

4. The hydrogenation of 2,4-dimethylcyclopentene-1. a) In acid medium in the presence of platinized carbon. 35 g of the unsaturated hydrocarbon, 30 ml of ethyl alcohol, 1 g of powdered platinized carbon, 4 ml of a solution of chloroplatinic acid (0.1 g Pt in 1 ml of solution) and 10 ml of concentrated hydrochloric acid were shaken in a glass duck-shaped hydrogenation vessel for 2 hours. 8.1 liters of hydrogen (0°, 760 mm) were absorbed. This amounted to 0.99 mole per 1 mole of hydrocarbon. After removal from the alcoholic solution, treatment with concentrated sulfuric acid, washing with water, and drying, 33.6 g of the saturated hydrocarbon was obtained (94.1% of theory). Upon distillation in a column with the equivalent of 30 theoretical plates, it boiled at 90.5° (755 mm) and had n_D^{20} 1.4095, d_4^{20} 0.7454, found MR_D 32.57, computed 32.33, aniline point 48.5°.

b) In the vapor phase in the presence of platinized carbon at 160°. 31.5 g of the unsaturated hydrocarbon was passed at a space velocity of 0.2 in an excess of hydrogen through a glass tube filled with platinized carbon (20% Pt), which was placed in a tubular electric oven and heated to 160°C. After the usual treatment (see part a) the collected saturated hydrocarbon was distilled in a column with the equivalent of 30 theoretical plates. B.p. 90.4° (750 mm); n_D^{20} 1.4094; d_4^{20} 0.7454, found MR_D 32.57, computed 32.33, aniline point 48.5°.

In Table 2 are listed the properties of all the preparations of 1,3-dimethylcyclopentane obtained in the different experiments described in this work. Despite the differences in the conditions of preparation, they all have completely identical properties. The spectra of combined scattering of light, studied for them by M.I. Batuev, are also completely identical.

TABLE 2

Conditions of preparation	Properties of hydrocarbon						
	B.p.	Pressure mm Hg	n_D^{20}	d_4^{20}	MR _D found	MR _D calculated	aniline point
1. Direct hydrogenation of 2,4-dimethylcyclopenten-2-one	90.5°	751	1.4094	0.7457	32.56	32.33	48.5°
2. Hydrogenation of 2,4-dimethylcyclopentene-1 in acid medium	90.5	755	1.4095	0.7454	32.57	32.33	48.5
3. Hydrogenation of 2,4-dimethylcyclopentene-1 in vapor phase at 160°	90.4	750	1.4094	0.7454	32.57	32.33	48.5

The yield of 1,3-dimethylcyclopentane obtained by way of 2,4-dimethylcyclopentanol-1 and 2,4-dimethylcyclopentene-1, with the hydrogenation of the latter, amounted to 20-22% of theory, calculated on the basis of the starting material, dimethylvinylethynyl carbinol. In the work of Chavanne [3], cited above, the yield of 1,3-dimethylcyclopentane, calculated on the basis of the starting material, 1-methylcyclohexanol-4 (by way of β -methyladipic acid and β -methylcyclopentanone) also amounted to about 20%.

We take the occasion to express our thanks to M.I. Batuev and A.D. Matveeva for the optical investigation of the 1,3-dimethylcyclopentane preparations.

SUMMARY

1. 1,3-dimethylcyclopentane can be successfully synthesized starting with 2,4-dimethylcyclopenten-2-one-1 (by the method of Nazarov) from 2-methylhexan-5-ine-3 (dimethylvinylethynyl carbinol).

2. Despite the different conditions of synthesis of 1,3-dimethylcyclopentane, the preparations of it which were obtained had extremely close properties; this forces us to consider the question of its possible existence in stereoisomeric forms as a still-open one.

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INVESTIGATION IN THE DOMAIN OF POLYCYCLIC COMPOUNDS

XI. ON THE INFLUENCE OF THE COMPOSITION OF THE SUBSTITUENTS ON THE COLOR OF 1-AMINO-4-x-SUBSTITUTED ANTHRAQUINONES

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Despite the fact that modern electron theories make it possible to determine the causes of the colors of organic compounds fairly completely, the structure of the absorption spectra of colored compounds with regard to their composition and the structure of their molecules is still extremely difficult. Therefore, as before, the accumulation of empirical rules for the relationship of the colors of organic compounds to their structures is definitely necessary for a more detailed development of the foundations of this relationship.

Having devoted a number of preceding papers [1] to the synthesis and study of the properties of several polycyclic compounds, we decided at this time to investigate in addition the relationship between the colors of these compounds and their structures. With regard to this latter question, we found only very brief reports in the literature. Thus, R. Schmidt [2] found a qualitative relation between structure and color in a number of the simplest monosubstituted anthraquinones; M. Kunz, in a number of papers [3], gave fragmentary data on the relationships of the colors of the representatives of various groups of polycycloketones to their structures; similar material was presented by one of the present authors [4] in somewhat more systematic form. Similar data of a review nature can also be found in R. Thomson [5]. However, not one of the works cited has listed the corresponding experimental material. The necessary information, i.e., the determination of the absorption spectra, are provided only for several individual examples of the anthraquinone series by Formanek [6], but it is impossible to draw any general conclusions from them.

We decided to begin the study of this question with an investigation of the influence of various substituents on the colors of the simplest substituted polycycloketone - anthraquinone. The closest to the present paper are the data published by R. Schmidt [2]. This author found that the deepening of the color of α -substituted anthraquinones took place in a manner that depended on the following order of introduction of substituents: Cl, Br, NO₂, OH, SH, NH₂, NHC₆H₅. For the present work, we took as the object of our investigation the series of 4-x-substituted 1-aminoanthraquinones, and as the first step we decided to determine whether the observations of R. Schmidt on the influence of the substituents held true about them. The experimental data would have to determine to what extent the presence of an invariable second group influenced the order of succession of the substituents in the series given above. According to V.A. Izmailsky [7], the color of colored substances may be regarded as the result of the interaction of separate systems. In our case, the electrophilic quinone system

and the 1,4-bidonor system of the substituents might be considered the two interacting systems. The increased electrodonor capacity in comparison with that of the monosubstituted compounds was the characteristic we selected for the series of compounds, but it was necessary to assume that the order of influence of two substituents of which one was constant would correspond to the order of influence of single monosubstituents in the overall bathochrome shift. As substituents we chose the following groups: Cl, Br, NO₂, OH, OCH₃, NH₂, N(CH₃)₂, NHCOC₆H₅, and NHC₆H₅. The majority of the compounds with these substituents are well known in the literature. For this investigation, naturally, it was necessary to obtain them in chemically pure condition. For this purpose we utilized to some extent industrial products, whose purification at once resulted in chemically pure substances, but in most cases it was necessary to synthesize the desired compounds, and for this we endeavored, without reference to the yields, to choose methods of synthesis which would as much as possible exclude the formation of byproducts and thus facilitate to a considerable degree the purification of the substances synthesized.

TABLE

No. of Expt.	Name of substance	Wave length (mμ) corresponding to the maximum absorp- tion of measurement		Data of Form- anek	Shift (mμ) of absorp- tion maximum in long- wave direction com- pared with previous compound meas- ured	
		Chlorobenz- ene solu- tions	ethyl alcohol solu- tions		Chlorobenz- ene solu- tions	Ethyl al- cohol solutions
1	2	3	4	5	6	7
1	1-Aminoanthraquinone	460	475	-	-	-
2	1-Amino-4-nitroanthraquinone	460	474	-	0	1
3	1-Amino-4-chloroanthraquin- one	470	482	-	10	8
4	1-Amino-4-bromoanthraquinone	470	482	-	0	0
5	1-Amino-4-methoxyanthra- quinone	502	513	-	32	31
6	1-Amino-4-hydroxyanthra- quinone	520 } 550 }	525 } 556 }	529.4	18 -	12 -
7	1-Amino-4-benzoylaminoan- thraquinone	525 } 558 }	530 } 562 }	-	5 8	5 6
8	1,4-diaminoanthraquinone ..	535 } 568 }	541 } 584 }	584.5	10 10	11 22
9	1-Amino-4-dimethylamino- anthraquinone	565 } 605 }	565 } 604 }	-	30 32	24 20
10	1-Amino-4-phenylaminoan- thraquinone	565 } 604 }	565 } 606 }	-	0 1	0 2

Among the compounds synthesized were the following: 1) 1-amino-4-nitroanthraquinone, obtained from 1-benzoylaminoanthraquinone by nitration and subsequent saponification; 2) 1-amino-4-chloro- and 1-amino-4-bromoanthraquinone, by the Sandmeyer reaction from 1-benzoylamino-4-aminoanthraquinone [8]; 3) 1-amino-4-hydroxyanthraquinone, obtained under certain conditions [9] from 1-benzoylamino-4-hydroxyphenylene, and phthalic anhydride by the Friedel-Crafts reaction [10]; 4) 1-amino-4-dimethylamino- and 1-amino-4-phenylaminoanthraquinones, by the condensation of the 1-amino-4-bromo-2-sulfonic acid of anthraquinone with dimethylamine or aniline in the presence of copper sulfate, followed by the splitting off

of the sulfonic acid group in a manner similar to that given [11]. For the preparation of chemically pure 1-aminoanthraquinone, 1,4-diaminoanthraquinone, and 1-amino-4-benzoylaminoanthraquinone, we purified the industrial products. We obtained 1-amino-4-methoxyanthraquinone by the debenzoylation of the algal dye Aloe G (By) by the method of Ilyinsky and Zaikin [12]. The data listed below on yields of products may possibly be changed in the direction of increased yields as the result of additional investigation. This question, as has already been indicated above, did not interest us.

In order to explain the influence of one or another substituent on the color, we measured the maximum of the absorption spectra of these compounds and then found the value of the shift of the maximum when one substituent was replaced by another. The measurements were made on a Goldberg spectrodensograph. The measurements were carried out with solutions of the given compounds in chlorobenzene and in ethyl alcohol (see Figures 1 and 2 in Experimental section). We considered that the results obtained were preliminary, and we propose later to investigate the absorption spectra of our compounds also in the ultraviolet region. The results of the measurements permitted us to determine the displacement of the maxima of the absorption bands (Table 1).

Basing ourselves on the results obtained, we may arrange the substituents according to the extent of their deepening of the color in the following order. NO_2 , Cl, Br, OCH_3 , OH, NHCOC_6H_5 , NH_2 , $\text{N}(\text{CH}_3)_2$, NHC_6H_5 , which is thus different from Schmidt's order only for the first three substituents.

The authors convey their thanks to the collective of the analytical laboratory of the Institute of Organic Chemistry for carrying out the analyses of the compounds prepared.

EXPERIMENTAL

Preparation of chemically pure compounds 1) 1-Aminoanthraquinone. 1-Aminoanthraquinone was obtained from the technical product by sublimation in a current of oxygen. The sublimed product was in the form of red needles with m.p. 253.5-254.5°.

3.560 mg substance: 0.191 ml N_2 (21°, 757 mm).

4.770 mg substance: 0.252 ml N_2 (19°, 757 mm).

Found %: N 6.21, 6.15.

$\text{C}_{14}\text{H}_9\text{O}_2\text{N}$. Computed %: N 6.28.

2) 1-Amino-4-nitroanthraquinone. 1-Amino-4-nitroanthraquinone was prepared by the nitration of 1-benzoylaminoanthraquinone with a nitrating mixture at a temperature from +4 to +5°. The yield of 1-benzoylamino-4-nitroanthraquinone amounted on an average to 92% of the theoretically calculated amount. In order to obtain 1-amino-4-nitroanthraquinone, the product of nitration was heated for 30 minutes on a boiling water bath with sulfuric acid of sp. gr. 1.84 (5 ml acid per 1 g of starting substance). The free amine was purified by recrystallization from nitrobenzene, chlorobenzene, and acetic acid. The purified product was in the form of needles with a brick-red color, with m.p. 295°.

2.988 mg substance: 0.265 ml N_2 (21.5°, 743 mm).

3.553 mg substance: 0.323 ml N_2 (21.5°, 743 mm).

Found %: N 10.05, 10.30.

$\text{C}_{14}\text{H}_8\text{O}_4\text{N}_2$. Computed %: N 10.44.

3) 1-Amino-4-methoxyanthraquinone. 1-Amino-4-methoxyanthraquinone was obtained by the debenzoylation of the algal dye Aloe G (By) by heating to 100° for 10 minutes with sulfuric acid of sp. gr. 1.84 (4 ml acid per 1 g of original substance). The 1-amino-4-methoxyanthraquinone was obtained in a yield of 99%. It was purified by being transformed into the sulfate, and precipitated from the solution of amine in concentrated sulfuric acid first formed by being diluted until

the H_2SO_4 was 62%. To complete the purification, the amine was recrystallized from dilute acetic acid. It was obtained in the form of brown platelets, with m.p. 166.5-167.5°.

3.129 mg substance: 0.159 ml N_2 (22°, 751 mm).
3.320 mg substance: 0.167 ml N_2 (22.5°, 752 mm).

Found %: N 5.81, 5.74.

$\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$. Computed %: N 5.50.

4) 1-Amino-4-hydroxyanthraquinone. 1-Amino-4-hydroxyanthraquinone was obtained by heating benzoylamino-p-hydroxyphenylene and phthalic anhydride with a mixture of aluminum chloride and table salt. The 1-benzoylamino-4-hydroxyanthraquinone which was formed was purified by conversion into the leuco compound, followed by oxidation with hydrogen peroxide, and then by removal of the benzoyl group by heating the product with 100% sulfuric acid. The yield of 1-amino-4-hydroxyanthraquinone amounted on an average to 70% of the theoretical, calculated on the basis of the original benzoylamino-p-hydroxyphenylene. The final purification of the product obtained was carried out by recrystallization from chlorobenzene.

The purified substance was in the form of deep bronze platelets, m.p. 206.5-207.5°.

3.68 mg substance: 0.194 ml N_2 (22°, 745 mm).
3.10 mg substance: 0.158 ml N_2 (22°, 745 mm).

Found %: N 5.98, 5.78.

$\text{C}_{14}\text{H}_9\text{O}_3\text{N}$. Computed %: N 5.85.

5) 1,4-Diaminoanthraquinone. For the preparation of 1,4-diaminoanthraquinone, we sublimated the technical product. The substance was obtained in the form of needles with a blue-black color. Its melting point equaled 267-267.5°.

2.458 mg substance: 0.257 ml N_2 (23°, 736 mm).
0.403 mg substance: 0.403 ml N_2 (23°, 736 mm).

Found %: N 11.70, 11.68.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$. Computed %: N 11.76.

6) 1-Amino-4-benzoylaminoanthraquinone. 1-Amino-4-benzoylaminoanthraquinone was obtained from the technical product by recrystallization from xylene and chlorobenzene. The purified product was in the form of red-violet needles with m.p. 279.5-281°.

3.360 mg substance: 0.233 ml N_2 (19°, 748 mm).
3.500 mg substance: 0.245 ml N_2 (20°, 748 mm).

Found %: N 7.98, 8.03.

$\text{C}_{21}\text{H}_{14}\text{O}_2\text{N}_2$. Computed %: N 8.18.

7) 1-Amino-4-dimethylaminoanthraquinone. In order to obtain 1-amino-4-dimethylaminoanthraquinone, we first condensed the 1-amino-4-bromo-2-sulfonic acid of anthraquinone with an aqueous solution of dimethylamine in the presence of copper sulfate. The sulfonic acid group was removed by heating the condensation product with sodium hydrosulfite in an aqueous-alcoholic medium. The yield of technical product amounted to about 60% of the amount theoretically calculated. The purification of the 1-amino-4-dimethylaminoanthraquinone was carried out by two conversions to the hydrochloride by the action of gaseous HCl on a solution of the product in chlorobenzene (1.25). Blue needles were obtained with m.p. 159.5-161°.

3.566 mg substance: 0.341 ml N_2 (21.5°, 744 mm).

Found %: N 10.85.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$. Computed %: N 10.52.

8) 1-Amino-4-phenylaminoanthraquinone. For the synthesis of 1-amino-4-phenylaminoanthraquinone we first heated the 1-amino-4-bromo-2-sulfonic acid of

anthraquinone with aniline in the presence of copper sulfate. Then, in order to remove the sulfonic acid group from the compound obtained, we heated the latter in an aqueous-alcoholic medium with sodium hydrosulfite. We obtained a mixture of blue and black needles in a yield of about 60% of the theoretically possible amount. The purification was carried out by converting the substance into the sulfate. For this purpose, the impure 1-amino-4-phenylaminoanthraquinone was dissolved in sulfuric acid, with sp. gr. 1.84, in the ratio 1:3. When the acid was

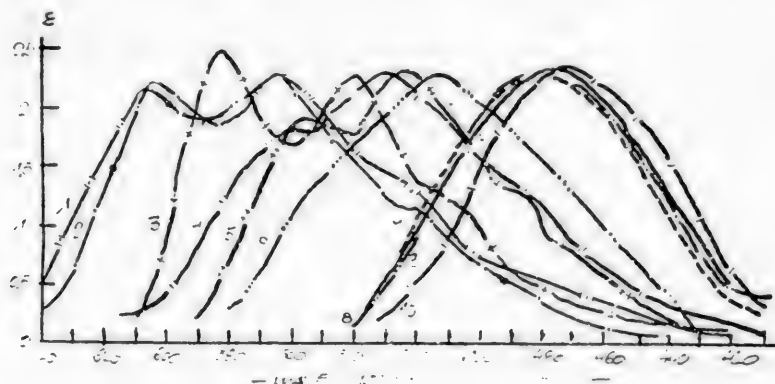


Fig. 1. Absorption curves of 1-NH₂-4-x-substituted anthraquinones in ethyl alcohol.

1-1-NH₂-4-NHC₆H₅-anthraquinone, 2-1-NH₂-4-N(CH₃)₂-anthraquinone 3-1-NH₂-4-NH₂-anthraquinone 4-1-NH₂-4-NHCOC₆H₅-anthraquinone 5-1-NH₂-4-OH-anthraquinone 6-1-NH₂-4-OCH₃-anthraquinone 7-1-NH₂-4-Br-anthraquinone, 8-1-NH₂-anthraquinone, 9-1-NH₂-4-Cl-anthraquinone, 10-1-NH₂-4-NO₂-anthraquinone.

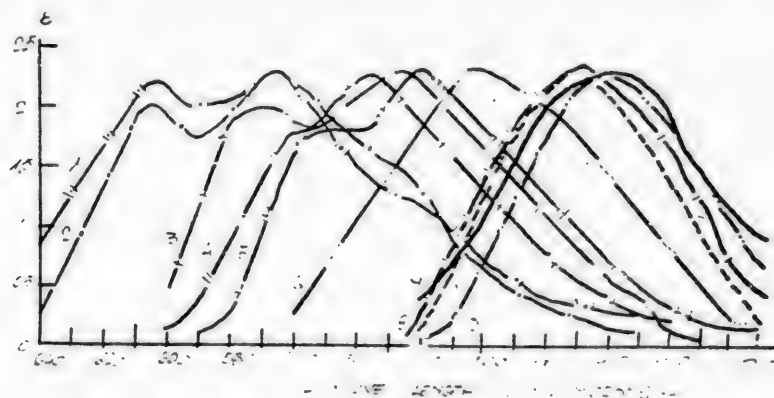


Fig. 2. Absorption curves of 1-NH₂-4-x-substituted anthraquinones in chlorobenzene.

1-1-NH₂-4-NHC₆H₅-anthraquinone, 2-1-NH₂-4-N(CH₃)₂-anthraquinone 3-1-NH₂-4-NH₂-anthraquinone 4-1-NH₂-4-NHCOC₆H₅-anthraquinone 5-1-NH₂-4-OH-anthraquinone 6-1-NH₂-4-OCH₃-anthraquinone 7-1-NH₂-anthraquinone 8-1-NH₂-4-Cl-anthraquinone; 9-1-NH₂-4-Br-anthraquinone 10-1-NH₂-4-NO₂-anthraquinone

diluted to a concentration of 50%, the sulfate precipitated. The substance was further purified by conversion into the hydrochloride under conditions similar to those described for 1-amino-4-diethylaminoanthraquinone. The product obtained was in the form of blue needles with m.p. 172.5-175°.

3.444 mg substance: 9.659 mg CO₂; 1.421 mg H₂O.
 3.155 mg substance: 8.862 mg CO₂; 1.271 mg H₂O.
 2.540 mg substance: 0.206 ml N₂ (19.5°, 746 mm).
 2.474 mg substance: 0.197 ml N₂ (21°, 747 mm).

Found %: C 76.53, 76.65; H 4.62, 4.51; N 9.29, 9.09.
 C₂₀H₁₄O₂N₂. Computed %: C 76.40; H 4.49; N 8.90.

Measurements of the absorption spectra. In Fig. 1 and Fig. 2, all the curves obtained for each solvent separately are brought together.

SUMMARY

1. Measurements of the absorption spectra of 1-amino-4-x-substituted anthraquinones (in the visible region) have permitted us to determine that their absorption maxima are displaced in the long wave direction when the second substituent is introduced in the following order. NO₂, Cl, Br, OCH₃, OH, NHCOC₆H₅, NH₂, N(CH₃)₂.^{NHC₆H₅} 2. The mutual arrangement of NO₂, Cl, and Br as substituents in this series differed, according to our data, from the results in Schmidt's work. This difference, which is in general very small, may apparently be explained by the different methods of investigating the compounds. Schmidt evaluated them visually, we used them for measurements with the Goldberg spectrodensograph.

3. In accordance with theoretical assumptions, the presence of one and the same second substituent in the 1,4-disubstituted anthraquinones had practically no influence on the sequence of arrangements of the absorption maxima of the spectra in the visible region, in comparison with the arrangements of the absorption maxima of the spectra for the analogous monosubstituted compounds.

4. All the 1-amino-4-x-substituted anthraquinones which contained OH and NH₂ groups as the second substituent, or derivatives of these, had two definite maxima in their absorption spectra, in contradistinction to the absorption spectra of the remaining 1,4-disubstituted anthraquinones, which had only a single maximum.

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⁷ See CB translation p. 755 ff.

INVESTIGATIONS IN THE DOMAIN OF POLYCYCLIC COMPOUNDS

XII. ON THE INFLUENCE OF THE COMPOSITION OF SUBSTITUENTS ON THE COLOR OF 1-BENZOYLAMINO-4-X-SUBSTITUTED ANTHRAQUINONES

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In a previous communication [1] we have published the results of measurements of the absorption spectra in the visible region of 1-amino-4-x-substituted anthraquinones. On the basis of these measurements, we were able to arrange the substituents according to the degree of their influence in deepening the color in the following order. NO_2 , Cl, Br, OCH_3 , OH, NHCOC_6H_5 , NH_2 , $\text{N}(\text{CH}_3)_2$, NHC_6H_5 . The present communication is devoted to the results of measurements of the absorption spectra of the analogous series of substituted 1-benzoylamino anthraquinones. The substituents were the same groups as in the 1-aminoanthraquinone series. All the compounds necessary for measurement were prepared for this work in chemically pure condition, just as in the previous investigation. Except for 1-benzoylamino-4-methoxyanthraquinone and 1,4-dibenzoylaminoanthraquinone, all the substances were synthesized from the corresponding 1-amino-4-x-substituted anthraquinones previously obtained by heating with benzoyl chloride and chlorobenzene [2,3]. The chlorobenzene solutions of the benzoylated compounds were measured on the Goldberg spectrodensograph (see Table and Figure in Experimental Section).

TABLE

Name of compound	Wave length (m μ) corresponding to absorption maximum	Data of Formanek obtained in xylene	Shift (m μ) of absorption maximum in long wave direction by comparison with preceding compound
1-Benzoylaminoanthraquinone	435	-	-
1-Benzoylamino-4-nitroanthraquinone .	435	-	0
1-Benzoylamino-4-chloroanthraquinone.	440	-	5
1-Benzoylamino-4-bromoanthraquinone..	441	-	1
1-Benzoylamino-4-methoxyanthraquinone	462	468.5	21
1-Benzoylamino-4-hydroxyanthraquinone	492	498.0	30
1,4-Dibenzoylaminoanthraquinone	498	508.5	6
1-Benzoylamino-4-aminoanthraquinone..	525	-	27
1-Benzoylamino-4-dimethylamino- anthraquinone	552	-	27
1-Benzoylamino-4-phenylamino- anthraquinone	551	-	1

The results of these measurements showed that the shift of the absorption maximum in the long-wave section of the spectrum takes place according to the same rule and in the same order as was found for 4-x-substituted 1-aminoanthraquinones. On the basis of these measurements we were able to arrange the substituents according to the extent of their influence in deepening the color in the following order: NO_2 , Cl, Br, OCH_3 , OH, NHCOC_6H_5 , NH_2 , $\text{N}(\text{CH}_3)_2$, NHC_6H_5 . This was identical with the order found in the previous communication.

EXPERIMENTAL

Preparation of chemically pure compounds. 1) 1-Benzoylaminoanthraquinone. 1-Benzoylaminoanthraquinone was obtained by the benzylation of 1-aminoanthraquinone in a yield of 92% of the theoretically possible amount. The product, recrystallized from aniline, was in the form of golden-yellow platelets with m.p. 254.5-255.5°.

4.340 mg substance: 0.165 ml N_2 (22°, 752 mm).

3.420 mg substance: 0.130 ml N_2 (22°, 745 mm).

Found %: N 4.39, 4.31.

$\text{C}_{21}\text{H}_{13}\text{O}_3\text{N}$. Computed %: N 4.28.

2) 1-Benzoylamino-4-nitroanthraquinone

To obtain 1-benzoylamino-4-nitroanthraquinone we nitrated 1-benzoylaminoanthraquinone under the usual conditions. The product obtained, after recrystallization from nitrobenzene, was in the form of badly formed crystals with a light yellow color and m.p. 280-281°.

2.861 mg substance: 0.189 ml N_2 (21.5°, 745 mm).

4.295 mg substance: 0.270 ml N_2 (18.5°, 748 mm).

Found %: N 7.51, 7.25.

$\text{C}_{21}\text{H}_{12}\text{O}_4\text{N}$. Computed %: N 7.52.

3) 1-Benzoylamino-4-methoxyanthraquinone. 1-Benzoylamino-4-methoxyanthraquinone was prepared by the recrystallization of the algal dye Aloe G (By) from xylene. After purification, the compound was in the form of platelets with a clear red color, with m.p. 245.4-246.4°.

4.140 mg substance: 0.147 ml N_2 (20°, 756 mm).

3.000 mg substance: 0.106 ml N_2 (21°, 756 mm).

Found %: N 4.11, 4.00.

$\text{C}_{22}\text{H}_{15}\text{O}_3\text{N}$. Computed %: N 3.91.

4) 1-Benzoylamino-4-hydroxyanthraquinone. In order to obtain 1-benzoylamino-4-hydroxyanthraquinone, we utilized the previously obtained 1-amino-4-hydroxyanthraquinone, which was heated with benzoyl chloride (1:4). The yield of benzylation product amounted to 80% of that theoretically calculated. After recrystallization from chlorobenzene, we obtained red-brown crystals with m.p. 253.5-254°.

3.820 mg substance: 0.132 ml N_2 (23°, 746 mm).

3.590 mg substance: 0.123 ml N_2 (23°, 746 mm).

Found %: N 3.91, 3.88.

$\text{C}_{21}\text{H}_{13}\text{O}_3\text{N}$. Computed %: N 4.08.

5) 1,4-Dibenzoylaminoanthraquinone. In order to prepare 1,4-dibenzoylaminoanthraquinone, we recrystallized the technical product from chlorobenzene (1:3). The yield of purified 1,4-dibenzoylaminoanthraquinone amounted to 60% of the amount used. The purified compound was in the form of red needles with m.p. 279-279.5°.

3.110 mg substance: 0.169 ml N_2 (19°, 729 mm).

3.600 mg substance: 0.204 ml N_2 (20°, 729 mm).

Found %: N 6.24, 6.33.

$\text{C}_{28}\text{H}_{18}\text{O}_4\text{N}_2$. Computed %: N 6.27.

6) 1-Benzoylamino-4-dimethylaminoanthraquinone. 1-Benzoylamino-4-dimethylaminoanthraquinone was obtained by heating 1-amino-4-dimethylaminoanthraquinone with benzoyl chloride in chlorobenzene (1:3). The amount of benzoyl chloride used was less than the calculated amount (95% of the theoretical), as our experiments showed that an excess of benzoyl chloride led to the formation of the dibenzoyl derivative. The yield of product obtained amounted to about 60% of that calculated theoretically. After recrystallization from chlorobenzene (1:5) we obtained blue needles with m.p. 172-174°.

2.519 mg substance: 0.158 ml N₂ (21°, 756 mm).

Found %: N 7.24.

C₂₃H₁₈O₃N₂. Computed %: N 7.53.

7) 1-Benzoylamino-4-phenylaminoanthraquinone. 1-Benzoylamino-4-phenylaminoanthraquinone was prepared by benzoylation of 1-amino-4-phenylaminoanthraquinone with a two-fold excess of benzoyl chloride. As solvent we used chlorobenzene (1:3). The yield of technical product amounted to 80%. The purified product was in the form of needles with a blue color, m.p. 195-197°.

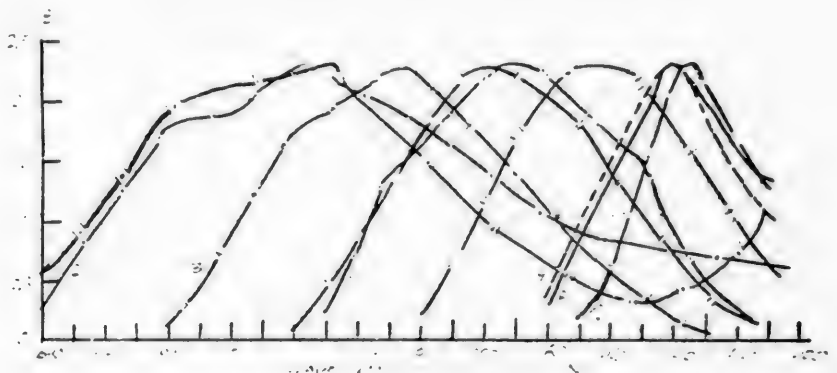
3.864 mg substance: 0.224 ml N₂ (22.5°, 752 mm).

2.549 mg substance: 0.146 ml N₂ (21.5°, 744 mm).

Found %: N 6.63, 6.51.

C₂₇H₁₈O₃N₂. Computed % N 6.69.

Measurements of the absorption spectra. The curves obtained for the absorption spectra are shown in the Figure.



Absorption curves of 1-benzoylamino-4-x-substituted anthraquinone in chlorobenzene

1-1-NHCO₆H₅-4-NHCO₆H₅-anthraquinone 2-1-NHCO₆H₅-4-N(CH₃)₂-anthraquinone 3-1-NHCO₆H₅-4-NH₂-anthraquinone
4-1-NHCO₆H₅-4-NHCO₆H₅-anthraquinone 5-1-NHCO₆H₅-4-OH-anthraquinone 6-1-NHCO₆H₅-4-OCF₃-anthraquinone
7-1-NHCO₆H₅-4-Br-anthraquinone 8-1-NHCO₆H₅-4-Cl-anthraquinone 9-1-NHCO₆H₅-anthraquinone 10-1-NHCO₆H₅-
4-anthraquinone.

SUMMARY

Measurements of the absorption spectra of 1-benzoylamino-4-x-substituted anthraquinones have proved that this series shows the same order of arrangement of the substituents with respect to their influence in deepening the color as the

series of 4-x-substituted 1-aminoanthraquinones and also, fundamentally, as the series of monosubstituted anthraquinones.

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* See CB translation p. 1567 ff.

** See CB translation p. 755 ff.

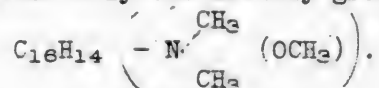
ON THE ALKALOIDS OF COCCULUS LAURIFOLIUS D.C.

II. ON THE STRUCTURE OF COCCULIDIN AND COCCULIN

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In a previous paper [1] we reported that Cocculus laurifolius D.C., grown in 1912 in the Batum region, did not contain cocclaurin. Instead of this, we were able to isolate from the leaves of this plant two new alkaloids, named cocculin, $C_{17}H_{21}NO_2$, and cocculidin $C_{18}H_{23}NO_2$. On the basis of a quantitative determination of the functional groups we gave formulas of the two alkaloids in a developed form. Upon methylation with diazomethane, cocculin, which is a base of a phenol character, gives another alkaloid of non-phenol character, cocculidin: $C_{16}H_{17}(>N-)(OCH_3)(OH) \rightarrow C_{16}H_{17}(>N-)(OCH_3)_2$. In sulfuric acid solution, cocculin and cocculidin easily decolorize permanganate, which indicates the presence of a double bond. Thus, after the determination of the structure of cocculidin, it remains for us to determine the position of the phenol hydroxyl in cocculin, which must occupy the position of one of the methoxy groups in cocculidin. Under the action of methyl iodide, cocculidin gives a splendidly crystalline methiodide with m.p. 239° . This methiodide easily and smoothly undergoes decomposition upon heating with a methyl alcohol solution of alkali according to Hofmann's method, and gives an optically active des-N-methylcocculidin $[(\alpha)_D + 108.89^\circ, \text{m.p. } 82-83^\circ]$. On the basis of a complete elementary analysis and the determination of the functional groups of des-N-methylcocculidin, the following composition and developed formula were found. $C_{19}H_{25}NO_2 = C_{16}H_{16}(>N-CH_3)(OCH_3)_2$. This des-base gave a crystalline methiodide, with m.p. 206° . Upon heating with alcoholic alkali, this did not split off trimethylamine. An optically inactive, viscous, colorless, oily base was obtained, which gave a crystalline hydrochloride with m.p. 196° . The des-N-dimethylcocculidin obtained had the composition $C_{19}H_{23}NO$, and instead of two methoxyls contained only one methoxy group,



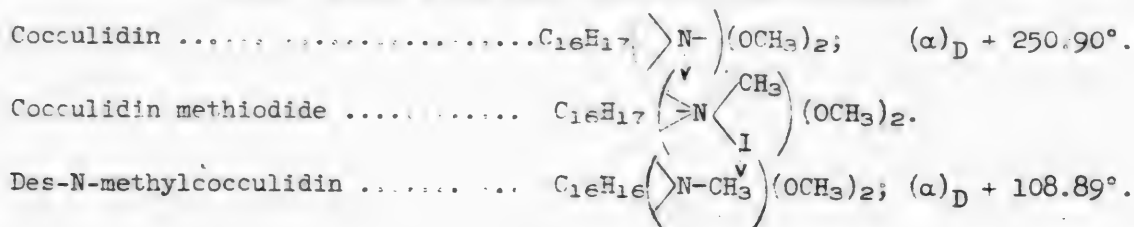
This fact showed that one methoxyl group had been split off in the form of methyl alcohol, and that it was in the ring which contained a double bond, that is, in the tetrahydrobenzene ring. Therefore we can assume that when in the second stage of decomposition a second double bond appeared, the ring became a dihydrobenzene ring. Later, as the result of splitting off methyl alcohol by means of the methoxyl group and one of the hydrogens next to it, a third double bond appeared, and the tetrahydrobenzene ring of cocculidin became completely aromatic. In des-N-dimethylcocculidin, apparently, there are no asymmetrical carbon atoms; in addition, this is the only reason which can explain the presence of one reactive double bond instead of two in des-N-dimethylcocculidin.

The Hofmann method of decomposition, as is known, always takes place with the rupture of the bond between the nitrogen and the carbons in several theoretically possible ways, with the formation of various isomers of the des-N-methyl base, and the final substance without nitrogen as usually obtained is not a single compound. In this case, both in the first stage of decomposition and in the second, in addition to the chief decomposition product described there was also the formation of other products, but because of their small amounts we did not undertake to separate them into individual isomers. In the expectation of obtaining the final nitrogen-free decomposition product of cocculidin as a single compound, we formed the methiodide of the non-individualized des-N-dimethylcocculidin. Upon heating with alcoholic alkali, the non-crystalline methiodide isomers split off trimethylamine. A viscous oily nitrogen-free substance was obtained, which darkened in the air fairly rapidly. The oxidation of this substance with potassium permanganate in acetone solution gave a crystalline acid $C_{15}H_{12}O_5$, with m.p. 189-190°. A quantitative determination of functional groups made it possible to break down the formula of this acid as follows: $C_{12}H_7(OCH_3)(COOH)_2$. This was confirmed by the formation of the crystalline dimethyl ester $C_{12}H_7(OCH_3)(COOCH_3)_2$. Hence it was necessary to assume that the nitrogen-free compound had the following formula. $C_{12}H_7(OCH_3)(-CH=CH_2)_2$. Upon oxidation, it lost two molecules of carbon with the formation of two molecules of formic acid and the dicarboxylic acid described above. As the nitrogen-free compound from cocculidin was obtained after the third stage of decomposition, it was necessary to expect that three active double bonds would be formed and the acid which corresponded to them. As can be seen from the formula, we obtained a dicarboxylic acid. This once more confirmed the fact that the production of an aromatic character in the tetrahydrobenzene ring of cocculidin took place in the second stage of decomposition. Therefore there remained the single possibility that one double bond of the three formed by decomposition was a bond of aromatic character.

In order to test the direction of decomposition of cocculidin, all the stages of decomposition were carried out at a lower temperature by the action of AgOH on the methiodide. In this case, the same course of decomposition was observed, with an aromatic character resulting at the second stage, and the same products being formed as were obtained in the case of the action of alcoholic KOH. We were therefore forced to draw the conclusion that the decomposition in stages and the splitting off of methoxyl were not the results of the secondary action of the alcoholic caustic potash, but were the normal course of the Hofmann degradation, with this system striving to assume an aromatic character. It is difficult therefore to assume that the disappearance of optical activity in the second stage of decomposition was the result of racemization which took place under the action of the reagents used.

Upon distilling the acid obtained from hemi-cocculidin with zinc dust, fluorene, $C_{13}H_{10}$, was obtained. If we imagine the methoxyl and carboxyl groups in the formula of the acid $C_{12}H_7(OCH_3)(COOH)_2$ replaced by hydrogens, we will have diphenyl, $C_{12}H_{10}$. Therefore, we may assume that the thirteenth carbon atom may have been obtained from the carboxyl group in position 2 in diphenyl. All the chemical and analytical data about cocculidin given above show that the acid obtained is diphenylmethoxy-dicarboxylic acid, and not a fluorene derivative.

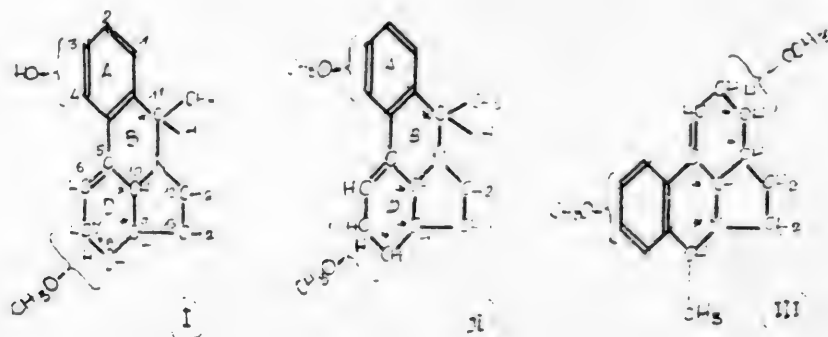
Scheme showing the decomposition of cocculidin



Des-N-methylcocculidin methiodide	$C_{15}H_{16} [\text{>N(CH}_3)_2 \text{I}] (\text{OCH}_3)_2$
Des-N dimethylcocculidin	$C_{16}H_{14} (\text{N(CH}_3)_2) (\text{OCH}_3)_3$
	\downarrow
Mixture of des-N-dimethylcocculidin methiodide isomers	$C_{16}H_{14} [\text{-N(CH}_3)_2 \text{I}] (\text{OCH}_3)$
	\downarrow
Nitrogen-free substance (hemcocculidin)	$C_{16}H_{13}(\text{OCH}_3) + \text{N(CH}_3)_3$
	or
	$C_{12}H_7(\text{CH=CH}_2)_2(\text{OCH}_3)_3$
Methoxydiphenyldicarboxylic acid	$C_{12}H_7(\text{COOH})_2(\text{OCH}_3)$

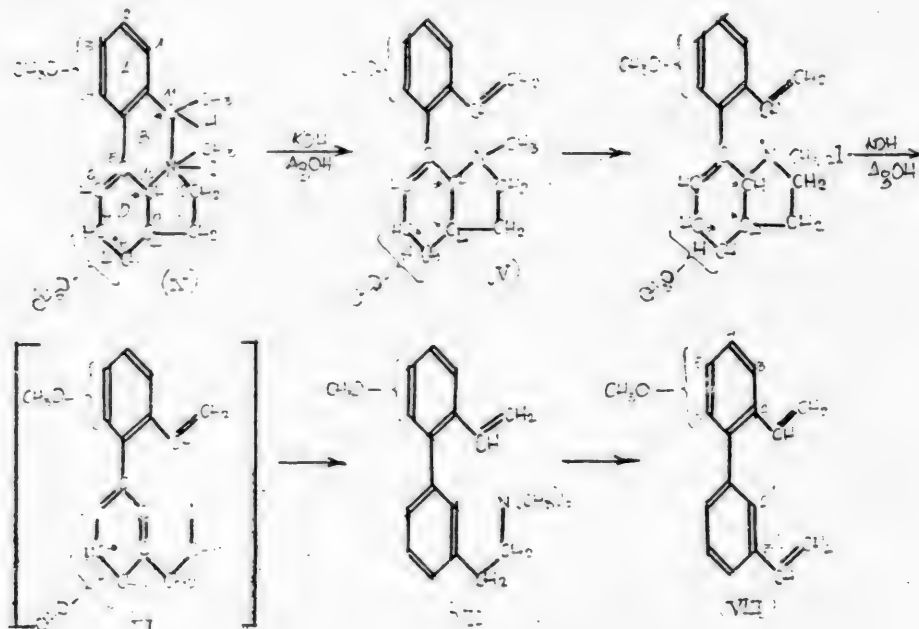
As the course of the Hofmann degradation showed, the nitrogen of cocculidin is split off in the form of trimethylamine only after the degradation is carried out three times. This shows that the nitrogen of cocculidin is bound in a bicyclic manner, i.e., it is at the point of juncture of two condensed rings. The easy and smooth course of all three steps in the degradation of cocculidin under the action of alcoholic alkali is characteristic of alkaloids which are derivatives of tetrahydroisoquinoline. On the other hand, cocculidin gives a positive reaction for pyrrol. Hence we must conclude that the heterocyclic condensed ring of cocculidin, on the one side, is piperidine, and on the other pyrrolidine. The splitting off of one of the methoxyl groups of cocculidin in the form of methyl alcohol shows that this methoxyl group was formed not from the phenol hydroxyl, but from the secondary alcohol hydroxyl. As methylation of cocculin, the base with a phenol character, gives cocculidin, it is clear that the sharply expressed phenolic hydroxyl group of cocculin is situated in the aromatic ring.

All the experimental results given above and the conclusions which have been drawn from them lead us to the formulas for cocculin (I) and cocculidin (II) directly below.

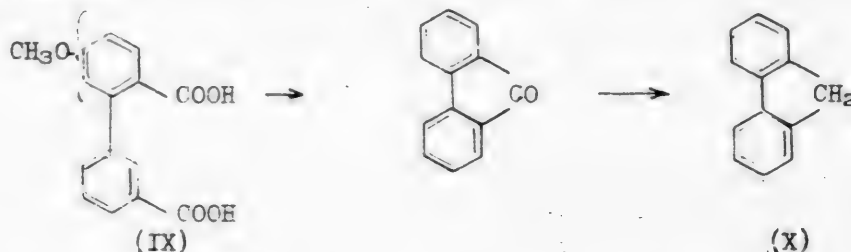


These formulas have not been decisively demonstrated experimentally in all details, but they are the most probable, and correspond to all the known chemical and optical properties of these alkaloids and their decomposition products. It is clear from formulas (I) and (II) that cocculin and cocculidin are derivatives of hexahydrophananthridine. If we write the formulas in the form (III), then the 1-methylisoquinoline half of the ring system is especially clearly seen. On the other hand, these compounds are indole derivatives, and their formulas to some extent recall part of the formula of strychnine; in addition both of them, especially cocculin, like strychnine, are highly toxic bases [2]. The

course of their degradation may be shown by the following equations:



The oxidation of methoxy-2,3'-divinyldiphenyl (hemi-cocculidin) (VIII) gives the corresponding acid with m.p. 190°, which upon distillation with zinc dust forms fluorene:



From a consideration of the formulas of cocculin and cocculidin it is easy to see that they contain four asymmetric carbon atoms. 7 or 8 (depending on the actual position of the methoxyl group), 9, 10, and 11 (designated by asterisks). The disappearance of the optical activity as a result of the Hofmann degradation may be the result of the fact that a double bond is formed near these asymmetric carbons. At the first stage of decomposition, it is chiefly the bond between carbon 11 and nitrogen that breaks, so that a double bond appears at this carbon and destroys one of the asymmetric centers. Thus, as a result of their decomposition, des-N-methylcocculidin (V) is obtained as the main product. If the rupture of the bond had taken place in another theoretically possible direction, to be specific, between carbon 10 and the nitrogen, then methyl alcohol would have split off at once because of the methoxyl, and the aromatic ring D would have been produced. If the decomposition had taken place with rupture of the link between the nitrogen atom and carbon 12, then after the second stage of decomposition (after ring D had become fully aromatic) carbon atom 11 would have kept its

asymmetry, i.e., des-N-dimethylcocculidin would have been optically active. But, as has already been indicated, the des-N-dimethylcocculidin formed is optically inactive. Thus, from all that has been said, we can conclude that the first stage of decomposition proceeds chiefly with a break of the bond between the nitrogen atom and carbon 11. In the second stage of decomposition, a double bond is formed between carbons 9 and 10, and the optical activity of carbons 9 and 10 is destroyed (VI). The appearance of a second double bond in the ring D increases the striving toward the completely aromatic character of this ring, and therefore the third double bond is easily formed in ring D as a result of the splitting off of methoxyl and of one hydrogen attached to carbons 7 or 8. As a result, ring D becomes aromatic, all four carbons lose their asymmetry, and the optically inactive des-N-dimethylcocculidin (VII) is formed. At the third stage, there remains a single possible direction for the formation of the double bond, between carbons 12 and 13. During this process, the des-N-dimethylcocculidin methiodide (the quaternary ammonium base) splits off trimethylamine to give methoxy-2,3'-divinyl-diphenyl (VIII).

As for the position of the double bond in the molecule of cocculin and cocculidin, it is obvious that this must be in a position in the ring D which is not destroyed during the decomposition, i.e., the positions between carbons 5 and 10, and 9 and 10 are excluded. On the basis of the smooth and easy course of the Hofmann decomposition, the splitting off of methoxyl and the acquisition of an aromatic nature by ring D, we may assume that the double bond is most probably at one of the two positions between carbons 5 and 6, or 7 and 8. If the first variant (5-6) is correct, then the methoxyl attached to ring D can have two possible positions, namely, at carbons 7 and 8. With the second variant (7-8), there is only the single position at carbon 6 for the methoxyl. The work on the determination of the position of the double bond and of the substituent groups of cocculin and cocculidin is being continued.

In our first communication [1] we showed that after the isolation of cocculidin (70% of the total amount of alkaloids) from the non-phenolic portion of the mixture of bases there remained another mixture of alkaloids (30%) which, because of its small amount, could not be separated into individual bases. Assuming that this mixture may possibly contain trimethylcocclaurin or methylarmepavine, we subjected it to the Hofmann degradation with the purpose of obtaining its decomposition products. As has now been learned, the nitrogen of cocculidin is at the juncture point of two condensed rings, i.e., it appears that the splitting off of nitrogen takes place only after the reaction has been carried out three times. The nitrogen of the tetrahydroisoquinoline alkaloids (with the group 1-methyl or benzyl tetrahydroisoquinoline, and others) splits off in the form of trimethylamine after the second stage of decomposition. Therefore, on the basis of this reaction we can determine the presence of alkaloids which are derivatives of tetrahydroisoquinoline in the mixture from which the cocculidin came. This tarry mixture gave a methiodide. The methiodide was heated with alcoholic alkali. The mixture of des-N-methyl bases obtained gave a methiodide, and this latter, upon heating with alcoholic alkali, split off trimethylamine. The nitrogen-free substance was separated from the des-N-dimethyl base. The crystalline hemi-product obtained was completely different from the nitrogen-free substance obtained from trimethylcocculidin and methylarmepavine. But this reaction showed clearly that the leaves of Cocculus laurifolius D.C. which we had investigated contained one more alkaloid of a non-phenolic nature - a derivative of 1-methyl or benzyl tetrahydroisoquinoline, and that this base constituted about 50% of the mixture left by the cocculidin. We hope that after accumulating sufficient amounts of this mixture from the cocculidin we shall be able to start the isolation of this alkaloid and decisively determine its structure.

The des-N-dimethyl base obtained after the second stage of decomposition

from the products left by the cocculidin, split off nitrogen after the third stage of decomposition to form a nitrogen-free product from which oxidation with potassium permanganate enabled us to obtain a methoxydiphenyldicarboxylic acid, identical with that obtained from hemi-cocculidin. Thus it became clear that the residue left by the cocculidin contained about 30% of cocculidin.

EXPERIMENTAL

The action of alcoholic KOH on cocculidin methiodide (des-N-methylcocculidin). 2 g of cocculidin methiodide with m.p. 238-239° was dissolved in 20 ml of methyl alcohol, 6 g of finely divided KOH was added to the solution, and the mixture was heated on the water bath for 1 hour. The alcohol was then driven off in a beaker on the boiling water bath. To the residue, 20 ml of water was added, and the base was thoroughly extracted with ether. After the ether had been driven off to leave a volume of 3 to 5 ml, the product was allowed to stand until the following day. Slow evaporation of the remaining ether resulted in the crystallization of the main portion. After recrystallization from petroleum ether, crystals precipitated in the form of fairly large prisms, m.p. 82-83° (a mixed test with cocculidin gave a lowering of the m.p. to 65°). The yield of the crystalline portion was 0.8 g, and the non-crystalline mixture of des-bases amounted to 0.4 g. Des-N-methylcocculidin was very soluble in alcohol, chloroform, and ether, more difficultly soluble in petroleum ether, insoluble in water.

0.1648 g substance. 12 ml methanol, $\bar{l} = 1.005$ dm, $\alpha = +1.5^\circ$
 $(\alpha)_D = +108.89^\circ$.

3.520 mg substance. 9.890 mg CO₂, 2.698 mg H₂O.
 3.788 mg substance. 10.675 mg CO₂, 2.950 mg H₂O. . . .
 4.560 mg substance. 0.202 ml N₂ (20°, 725 mm).
 4.460 mg substance. 0.195 ml N₂ (20°, 725 mm).
 9.455 mg substance. 3.77 ml 0.1 N Na₂S₂O₃.
 8.800 mg substance. 1.73 ml 0.1 N Na₂S₂O₃.
 21.16 mg substance. 4.25 ml 0.1 N Na₂S₂O₃.

Found %. C 76.63, 76.86, H 8.58, 8.71.
 N 4.92, 4.86; OCH₃ 20.79, 20.35,
 NCH₃ 9.71.

C₁₉H₂₅NO₂. Computed %. C 76.25, H 8.36, N 4.68; OCH₃ 20.74,
 NCH₃ 9.7.

The action of AgOH on cocculidin methiodide. To 2 g of cocculidin methiodide, dissolved in 50 ml of water, there was added the freshly precipitated Ag₂O prepared from 0.8 g of AgNO₃, and the mixture was shaken for 30 minutes, until the solution no longer gave a reaction for halogen. The precipitate was filtered off, and the water driven off in a vacuum at 60° until the residue was dry. 15 ml of water were added to the residue, and the base was thoroughly extracted with ether. The solution was dried with anhydrous potash and concentrated to a small volume (3-5 ml). Upon slow volatilization of the ether, at room temperature, the residue almost completely crystallized. Yield 1.2 g. After recrystallization from petroleum ether, it had m.p. 82-83°. Yield 1 g. A mixed test with des-N-methylcocculidin obtained by the method described above gave no depression of the melting point.

The methiodide of des-N-methylcocculidin. 2 g of des-N-methylcocculidin with m.p. 82-83° were dissolved in 10 ml of methyl alcohol, and 2 ml of methyl iodide were added to the solution, which was boiled with a reflux condenser for 2 hours. The solvent was then driven off to leave a volume of 2-3 ml, and this was allowed to stand until the following day. During this standing a crystalline precipitate formed, and after cooling with ice, this was filtered off with suction. Yield 2.2 g. After recrystallization from methyl alcohol, the methiodide of des-N-methylcocculidin was obtained in the form of fine needle-shaped crystals

with m.p. 205-206°.

The action of KOH and AgOH on the methiodide of des-N-methylcocculidin.
3 g of the methiodide of des-N-methylcocculidin were dissolved in 50 ml of methyl alcohol, and 15 g of finely divided KOH was added to the solution, which was boiled on the water bath with a reflux condenser for 6 hours. Then the alcohol was driven off to leave a dry residue. During this process, no separation of trimethylamine was observed. To the residue there was added 25 ml of water, and the oily base which separated was thoroughly extracted with ether. The extract was dried over anhydrous potash. After the solvent had been driven off, there remained 2 g of a viscous oil with a greenish yellow color. The des-N-dimethylcocculidin distilled at 156-158° at 2 mm to give a completely colorless oil which gave a crystalline hydrochloride. In the air it darkened fairly readily. It had the odor of a base, and was optically inactive.

To the aqueous solution of the methiodide of des-N-methylcocculidin there was added the calculated amount of freshly precipitated Ag₂O. After complete precipitation of the iodide ions, the water was driven out of the filtered solution in a vacuum at 60-70°. The product of reaction was extracted with ether. After the ether had been driven off, the des-N-dimethylcocculidin was obtained in the form of a viscous oil which boiled at 156-158° at 2 mm ($\alpha = +0^\circ$), and was identical with that obtained by the action of KOH on the methiodide of des-N-methylcocculidin.

3.012 mg substance. 8.966 mg CO₂; 2.334 mg H₂O.
3.452 mg substance. 10.205 mg CO₂; 2.590 mg H₂O.
5.472 mg substance. 16.228 mg CO₂; 4.228 mg H₂O.
4.500 mg substance. 0.219 ml N₂ (30°, 718 mm).
6.700 mg substance. 0.399 ml N₂ (23°, 722 mm).
26.665 mg substance. 6.34 ml 0.1 N Na₂S₂O₃.
21.605 mg substance. 5.27 ml 0.1 N Na₂S₂O₃.
Found %: C 81.18, 80.62, 80.88; H 8.67, 8.40,
8.65; N 4.95, 5.24; OCH₃ 12.29, 12.61.
C₁₉H₂₃NO. Computed %: C 81.14, H 8.19; N 4.98; OCH₃ 11.03.

The hydrochloride of des-N-dimethylcocculidin. To a saturated acetone solution of the base, a concentrated alcoholic solution of hydrochloric acid was added until there was complete neutralization. During this process, the hydrochloride of des-N-dimethylcocculidin precipitated in the form of shining silky crystals with m.p. 195-196°. Upon further recrystallization from acetone and from alcohol, the melting point remained unchanged.

0.1890 g substance: 6.00 ml 0.1 N AgNO₃.
Found %: Cl 11.27.
C₁₉H₂₃NO·HCl. Computed %: Cl 11.18.

The action of KOH and AgOH on the methiodide of des-N-dimethylcocculidin.
4 g of des-N-dimethylcocculidin were dissolved in 25 ml of methyl alcohol, and to the solution there was added 5 ml of methyl iodide. The mixture was then heated on the water bath for 6 hours, and the solvent then driven off completely. To the residue there was added 15 g of KOH and 50 ml of methyl alcohol, whereupon, even during the mixing, the formation of trimethylamine was observed. The mixture was heated on the water bath for 4 hours, until the formation of trimethylamine was complete. The alcohol was driven off to leave a dry residue, to which 50 ml of water was added, and the reaction product was repeatedly extracted with ether. The ether extract was washed with 5% sulfuric acid, then with water, and dried over anhydrous potash. After the ether had been driven off, a nitrogen-free product remained in the form of a viscous almost colorless oil, b.p. 218° at 2 mm. Yield 2 g. The nitrogen-free product was very soluble in almost all the usual organic solvents, it darkened in air, and had $\alpha = 0^\circ$. The sulfuric

acid wash solution was made alkaline with a saturated solution of alkali and extracted with ether to recover 0.2 g of the base, which gave a hydrochloride with m.p. 194-195°. A mixed test with the hydrochloride of des-N-dimethylcocculidin gave no lowering of the melting point. The same nitrogen-free product was obtained by treating the aqueous solution of the methiodide of des-N-dimethylcocculidin with silver oxide.

The oxidation of the nitrogen-free product. 2 g of the nitrogen-free product, which was not distilled in vacuum, were dissolved in 200 ml of acetone which had first been treated with permanganate. To the solution, at a temperature of 23-25° and with continuous stirring there were added 12 g of fine powdered KMnO_4 . Decolorization at first took place very quickly, and then slowed down. After the entire amount of permanganate had been added (2 hours) the solution was boiled for 4 hours. Then the excess of KMnO_4 was removed with methyl alcohol. The precipitate of manganese dioxide and potassium salt of the acid was filtered off. The acetone mother-liquor (A) was obtained completely colorless. The precipitate on the filter was washed with 100 ml of 1% caustic potash solution. Upon cooling, the alkaline solution was acidified with 50% sulfuric acid, and the precipitated acid was extracted with ether. After the ether had been driven off and traces of water had been removed in vacuum, 1.8 g of a cinnamon-colored semi-solid mass was obtained. To this residue, 2 ml of chloroform was added, and the residue was allowed to stand until the following day. This resulted in the precipitation of white finely needle-shaped crystals, which were filtered with suction and washed with a small amount of chloroform. M.p. 185-187°. Yield 1.1 g. The mother liquor gave an additional 0.1 g of substance. After the chloroform had been removed from the mother-liquor, there remained 0.6 g of a brown mass (B). The acetone was driven off from the acetone mother-liquor (A) to leave a small volume, and the residue was poured into a beaker. After the complete volatilization of the acetone, the residue was acidified and the precipitate extracted with ether. The ether was driven off to leave 0.2 g of a pale yellow viscous oil, which could not be crystallized in any way. These 0.2 g of viscous oil and the 0.6 g of mother-liquor (B) were united and dissolved in 50 ml of acetone, and to the solution there was added 6 g of finely powdered KMnO_4 . After boiling 4 hours, the excess KMnO_4 was removed with ethyl alcohol, the precipitated MnO_2 and the acid salts were treated with hot water, and 0.3 g of acid was obtained, identical with that indicated above. Thus, 2 g of the nitrogen-free product gave a total of 1.5 g of crystalline acid with m.p. 185-187° (0.6 g of nitrogen-free substance gave 5 g of the same acid). After two recrystallizations from ether, the melting point of the acid was raised to 189-190°. Upon further recrystallization, there was no change in the melting point. The crystals were obtained from chloroform in the form of long needles, and from ether in the form of prisms. The acid obtained was readily soluble in methyl and ethyl alcohols and in acetone, more difficultly soluble in ether and in chloroform, almost insoluble in water. $\alpha \pm 0^\circ$.

0.1248 g substance. 0.3030 g CO_2 , 0.0502 g H_2O .
 0.1248 g substance. 0.3118 g CO_2 , 0.0556 g H_2O .
 3.930 mg substance. 9.590 mg CO_2 , 1.598 mg H_2O .
 12.670 mg substance. 27.56 ml 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$.
 10.290 mg substance. 22.40 ml 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$.
 7.160 mg substance. 5.20 ml 0.01 N NaOH .
 8.040 mg substance. 5.84 ml 0.01 N NaOH .

Found %: C 66.22, 66.29, 66.55, H 4.50, - 84, 4.55, OCH_3 11.25, M 272.2, 275.2
 $\text{C}_{15}\text{H}_{12}\text{O}_5$. Computed %: C 66.18, H 4.41, OCH_3 11.39, M 272.

The dimethyl ester of the acid. 0.4 g of the acid with m.p. 189-190°, obtained from the nitrogen-free product, was dissolved in anhydrous ether, and an ether solution of diazomethane obtained from 5 g of nitrosomethylurea was added. Thereupon a vigorous reaction took place, with the evolution of nitrogen. The mixture was allowed to stand until the following day. The ether was then completely

driven off. There remained a colorless viscous oil, which crystallized after distillation in vacuum (1-2 mm). After recrystallization from petroleum ether, fine prisms precipitated, arranged in the form of round masses. M.p. 73-74°. Yield 0.3 g. The dimethyl ester of the acid was readily soluble in alcohol, acetone, and ether, more difficultly soluble in petroleum ether.

3.305 mg substance: 8.245 mg CO₂; 1.560 mg H₂O.

4.070 mg substance: 10.175 mg CO₂; 1.903 mg H₂O.

Found %: C 68.04, 68.18; H 5.28, 5.23.

C₁₇H₁₈O₅. Computed %: C 68.00; H 5.33.

The distillation of the acid with zinc dust. 0.7 g of the acid was dissolved in 5 ml of ethyl alcohol and the solution mixed with 100 g of zinc dust. The alcohol was completely driven off on the water bath. The mixture was placed in a tube sealed at one end, about 400 mm long and with inner diameter 12 mm, and another 100 g of pure zinc dust was added. At first that part of the tube where the pure zinc dust was placed was heated to a faint incandescence, then the part of the tube containing the compound was heated. After the reaction tube had cooled, the distillation products partially crystallized at the end of the tube and in the receiver which was cooled with ice. The entire tube and the zinc dust were washed with ether and the distillate collected in the receiver was dissolved in this ether. The ether solution, the extracts of all the reaction product, was washed with 3% KOH in water, then dried with potash, and the ether completely driven off. The residue was dissolved in 15 ml of methyl alcohol and treated with animal charcoal. The filtered solution was concentrated to a volume of 2 ml. Thereupon fine crystals precipitated, with m.p. 104-107°. Yield 0.3 g. After recrystallization from methyl alcohol, the melting point of the crystals rose to 113-114°. Yield 0.15 g. A mixed test with fluorene (m.p. 115°) gave no lowering of the melting point.

2.936 mg substance: 10.092 mg CO₂; 1.640 mg H₂O.

4.48 mg substance: 15.154 mg CO₂; 2.460 mg H₂O.

Found %: C 93.75, 93.55; H 6.25, 6.23.

C₁₃H₁₀. Computed %: C 93.97, H 6.03.

SUMMARY

1. The first stage of the Hofmann degradation of cocculidin, under the action of KOH and AgOH, takes place in the same manner as with 1-substituted tetrahydroisoquinoline alkaloids, with the formation of optically active des-N-methylcocculidin. In this reaction, the chief result is the opening of ring B, with the destruction of the asymmetry of carbon 11.

2. At the second stage of the degradation, carried out by the action of KOH or AgOH, a double bond is formed chiefly between carbons 9 and 10. After the appearance of this second double bond in ring D, methyl alcohol is split off because of the methoxyl group and one hydrogen, and the ring acquires an aromatic nature.

Thus, after the second stage of the degradation, all four carbon atoms have lost their asymmetry, and optically inactive des-N-dimethylcocculidin is obtained, containing a single methoxyl and a single vinyl group.

3. After the third stage of the degradation, a nitrogen-free substance is formed, methoxy-2,3'-divinyldiphenyl, whose formula was confirmed by its conversion into methoxydiphenyl-2,3'-dicarboxylic acid and the latter's dimethyl ester.

4. The distillation of the acid with zinc dust gives fluorene. The five-membered ring of the latter is formed, apparently, from the carboxyl group in

position 2.

5. The course of the Hofmann degradation shows that the nitrogen of cocculin and cocculidin is at the point of juncture of two condensed rings, on the one side a pyrrolidine, and on the other a piperidine ring.

6. The phenolic hydroxyl group of cocculin is attached to the aromatic ring, A. The double bond and the methoxyl group are in ring D. They are not displaced during the degradation. A review of all the theoretically possible ways of decomposition of cocculidin permits us to assume that the double bond is in positions 5-6 or 7-8.

7. These facts show that cocculin and cocculidin are on the one hand derivatives of phenanthridine and on the other hand of indole, i.e., they are indophenanthridines.

8. On the basis of the products of the Hofmann degradation of the mother-liquor of cocculidin, it has been found that this tarry mother-liquor contains in addition to cocculidin (30%) still a third alkaloid (50% of the mother-liquor) of a non-phenolic nature, a derivative of 1-methyl or benzyltetrahydroisoquinoline

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* See CB translation p. 391 ff

THE INVESTIGATION OF THE ALKALOIDS OF NANOPHYTON ERINACEUM

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The presence of alkaloids in the plant Nanophyton erinaceum, which belongs to the family Chenopodiaceae, was determined by P.S. Massagetov. He collected the plant material which was used for this investigation. We found first of all that the alkaloids of this plant, which were obtained by the usual extraction with dichloroethane, readily distilled with steam, without leaving a residue. Therefore, in order to prepare them later we did not employ extraction of the plants, but simply distilled the alkaloids with steam from the crushed plant which had first been treated with a solution of caustic soda. As a result of this operation, from 15 kg of plant we obtained 16 g of a colorless mobile, strongly basic oil, which boiled at ordinary pressures within a wide interval 130-155°. This mixture of bases was fractionated with a dephlegmator. This gave two fractions with boiling ranges 132-140 and 140-154°. The first fraction gave a hydrochloride, which after recrystallization from alcohol was in the form of a well-crystallized optically active substance ($[\alpha]_D + 15.1^\circ$) with m.p. 253-254°. The elementary analyses of this hydrochloride corresponded well to the composition $C_7H_{15}N \cdot HCl$. The base obtained by us distilled at 133-135° and had a saturated character. In order to elucidate the structure of this base, it was dehydrogenated by heating with silver acetate by Tafel's method [1]. As a result we obtained a weak base which distilled at 142-143°. From this we obtained the picrate with m.p. 159-160°, the chloraurate with m.p. 125-126°, and the phthalate, with m.p. 117-119°. As these melting points almost coincided with the melting points of the corresponding salts of 2,6-dimethylpyridine [2], in order conclusively to settle this question we determined the melting points in mixed tests of these salts with the corresponding salts of the latter. During these tests, no lowering of the melting points was observed. It followed from this that the dehydrogenation product was 2,6-dimethylpyridine. The alkaloid itself must then be the optically active form of 2,6-dimethylpiperidine.

Starting from the assumption that the second plant alkaloid, which was responsible for the extended boiling range of the crude mixture, was 1,2,6-trimethylpiperidine, we separated a second, higher-boiling fraction, as well as the mixture of alkaloids which remained in the mother liquor after the crystallization of the hydrochloride of 2,6-dimethylpiperidine, by the action of nitrous acid. Under this action, in fact, only part of the base gave a nitrosamine, from which, as the result of heating with hydrochloric acid, we recovered optically active 2,6-dimethylpiperidine. Part of this mixture remained unchanged. From the unchanged portion we obtained a crystalline, optically active hydrochloride ($[\alpha]_D - 10.8^\circ$), which melted at 162.5-164°. The base obtained from this distilled at 153-154°. In order to show that this base actually was the optically active form of 1,2,6-trimethylpiperidine, the 1-2,6-dimethylpiperidine obtained

previously was methylated with formaldehyde in the presence of formic acid. This gave a substance identical with the base with m.p. 153-154°. Thus we may consider it strictly proved that the alkaloids of *Nanophyton erinaceum* are optically active forms of 2,6-dimethylpiperidine and 1,2,6-trimethylpiperidine, the plant content of the first being approximately four times as great as that of the second. The plant does not, apparently, contain other bases. Both these bases have already been described in the literature [3] in their racemic forms, but the attempts to separate them into optical antipodes have not met with success [4]. The optical activity of these bases shows that they are trans forms. This follows from the fact that the cis forms would correspond to meso forms, which would exclude the possibility of optical activity. The fact remains to be noted that this is the first time that bases with this structure have been found in plants.

EXPERIMENTAL

Isolation of the alkaloids. 15 kg of air-dried ground parts of the plants were treated with a 5% solution of caustic soda, placed in a vat fed with live steam, and a current of steam passed through until the distillate no longer gave a reaction with silicotungstic acid. In order to obtain a more concentrated solution, the collected distillate was made alkaline with solid caustic soda, and the alkaloids distilled from it with steam. This operation was repeated twice, thus making it possible to decrease considerably the volume of the solution, to approximately 200 ml. The solution was acidified with a concentrated solution of hydrochloric acid and extracted with ether in order to purify it from substances of a non-basic nature. The solution was then treated with a 50% caustic potash solution. The base, which separated in the form of a faintly colored oil, was extracted with ether. The ether solution of the base was dried with caustic potash, and the ether driven off. The oil which remained was fractionated with a dephegmator at ordinary pressure. This resulted in the collection of two fractions, distilling from 132-140° (12 g) and from 140-150° (4 g).

The purification of the first fraction (preparation of 1-2,6-dimethylpiperidine). 12 g of the first basic fraction with boiling range 132-140° was dissolved in dry ether, and to the solution an alcoholic solution of hydrogen chloride was added until there was an acid reaction to Congo red. The crystalline precipitate (15 g) was recrystallized twice from absolute alcohol. 6 g of substance was obtained, with m.p. 253-254°.

0.2073 g substance: 1 ml water; $\underline{1} = 0.5$ dm, $\alpha_D + 1.56^\circ$;
 $[\alpha]_D + 15.1^\circ$.

4.375 mg substance: 9.019 mg CO₂; 4.202 mg H₂O.

3.358 mg substance: 6.909 mg CO₂; 3.235 mg H₂O.

4.681 mg substance: 4.528 mg AgCl.

7.035 mg substance: 6.832 mg AgCl.

4.935 mg substance: 0.423 ml N₂ (22°, 726 mm).

Found %: C 56.22, 56.11; H 10.75, 10.78;

Cl 23.93, 24.02; N 9.47.

C₇H₁₅N·HCl. Computed %: C 56.18; H 10.78; Cl 23.70; N 9.36.

This hydrochloride gave the base by the usual method. The base distilled at 133-135° and had the following constants. d_4^{20} 0.8409; n_D^{20} 1.4442; α_D -5.80° without a solvent, $\underline{1}$ 0.5 dm, $[\alpha]_D$ -13.8°; MR_D found 35.76, computed for 2,6-dimethylpiperidine 35.92.

The dehydrogenation of the base with b.p. 133-135°. 3 g of the base, 36 g of silver acetate, 1.6 g of glacial acetic acid, and 26 ml of water were placed in a glass tube. The latter was sealed and heated for 6 hours at 180°. After the tube was opened, its contents were combined and filtered off from the metallic silver formed. The filtrate was treated with an excess of a 40% caustic soda

solution, and the base that separated was distilled with steam. The distillate was acidified with hydrochloric acid to bromothymol blue and extracted with ether. The ether solution was dried with potash and the ether driven off. The residue was a weak base, and most of it distilled over at 142-143°. The distilled product gave the following salts: the picrate, with m.p. 159-160°, the chloraurate with m.p. 125-126°, and the phthalate with m.p. 117-119°. These salts were directly compared with the corresponding salts of 2,6-dimethylpyridine, prepared from the synthetically obtained base. This comparison established their complete identity.

The separation of the alkaloids by the action of nitrous acid. From 4 g of the basic second fraction (boiling range 140-154°) in ether solution, under the conditions already described for the first fraction, the hydrochloride was obtained. This was combined, without recrystallization, with the crystalline mixture of hydrochlorides obtained by concentrating the alcoholic mother-liquors which remained after the recrystallization of the 2,6-dimethylpiperidine hydrochloride. 12 g of this mixture and 16 g of sodium nitrite were dissolved in 45 ml of water, and the solution was heated for 30 minutes on the boiling water bath. The cooled solution was acidified with hydrochloric acid (to methyl orange) and extracted several times with ether. The ether solution was dried with potash and the ether driven off. The residue was distilled in vacuum. 6.5 g of a substance which distilled at 102-103° (8 mm) was obtained.

2.379 g substance: 0.414 ml N₂ (24°, 734 mm).

Found %: N 19.32.

C₇H₁₄N₂O Computed %: N 19.72.

From this nitrosamine, by heating with hydrochloric acid, we recovered the base, which was identical with the previously obtained 1,2,6-dimethylpiperidine. The mother-liquor which remained after the extraction of the nitrosamine was treated with an excess of 50% caustic potash solution. The base which separated was distilled with steam. The distillate was acidified to Congo red with hydrochloric acid and evaporated to dryness in vacuum. The crystalline precipitate was recrystallized several times from dry acetone. 2.5 g of substance with m.p. 162.5-164° were obtained. This hydrochloride was considerably more soluble in alcohol than the hydrochloride of the previously obtained 1,2,6-dimethylpiperidine.

0.2471 g substance: 1 ml water; \bar{d}_4^{20} 0.5 dm; α_D -1.33°;
[α]_D -10.8°.

3.556 g substance. 7.650 mg CO₂; 3.547 mg H₂O.

5.003 g substance. 10.761 mg CO₂; 4.996 mg H₂O.

6.408 g substance: 5.554 mg AgCl.

Found %: C 58.67, 58.66; H 11.16, 11.17; Cl 21.44.

C₈H₁₇N HCl. Computed %: C 58.69, H 11.08, Cl 21.66.

This hydrochloride, in the usual manner, gave the base, which distilled at 153-154° and had the following constants: \bar{d}_4^{20} 0.8448; n_D^{20} 1.4485; α_D -18.17° without a solvent, \bar{d}_4^{20} 0.5 dm, [α]_D 43.02°, MR_D found 40.34, computed for 1,2,6-trimethylpiperidine 40.88.

The methylation of the base with b.p. 133-135° (1,2,6-dimethylpiperidine). 3 g of the base, 30 ml of a 30% aqueous solution of formaldehyde, and 11 g of formic acid were heated for 3 hours with a reflux condenser on a boiling water bath. At the beginning of heating, a vigorous evolution of carbon dioxide was observed. The cooled solution was treated with a small excess of hydrochloric acid and the water was completely driven off in vacuum. The dry residue was recrystallized from acetone. This gave the hydrochloride with m.p. 162.5-164°, identical with the hydrochloride of the tertiary amine previously obtained by nitrosation of the alkaloid mixture.

SUMMARY

From the above-ground portions of Nanophyton erinaceum, 1-2,6-dimethylpiperidine and 1-1,2,6-trimethylpiperidine were isolated. The total content of these bases in the plant was approximately equal to 0.1%. The content of the secondary amine was approximately 4 times as great as the content of the tertiary.

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December 20, 1948.



Roentgenogram of Potassium Bronze

Complex Compounds of Iron, Aluminum and Chromium with Pyramidon p. 1469

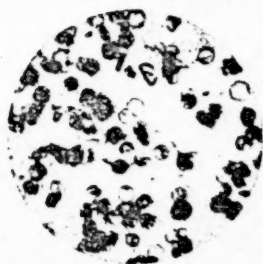


Fig. 1

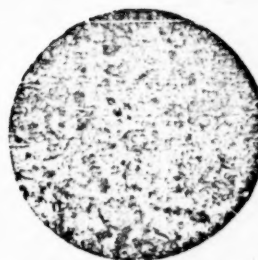
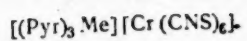
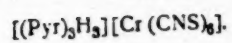


Fig. 2



continued from inside front cover

		page	Russ. page
28.	Investigations in the Domain of Polycyclic Compounds. XI. On the Influence of the substituents on the Color of 1-Amino 4-x Substituted Anthraquinones. <u>A. M. Lukin and K. K. Mozgova</u>	1567	1504
29.	Investigations in the Domain of Polycyclic Compounds. XII. On the Influence of the Composition of Substituents on the Color of 1-Benzoylamino-4-x-Substituted Anthraquinones. <u>A. M. Lukin and K. K. Mozgova</u>	1573	1510
30.	On the Alkaloids of <u>Cocculus Laurifolius</u> D.C. II. On the Structure of Cocculidin and Cocculin. <u>S. Yunusov</u>	1577	1514
31.	Investigation of the Alkaloids of Nanophyton Erinaceum. <u>A. D. Kuzuvkov and G. P. Mersnikov</u>	1587	1524

